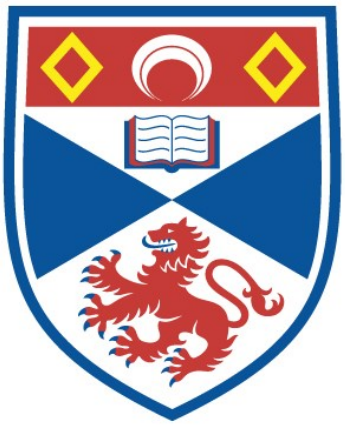
THE DESIGN OF CONDUCTING POLYMERS WITH METAL BINDING SITES

Sean Higgins

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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University of St. Andrews

School of Chemistry

The Design of Conducting Polymers with Metal Binding Sites

A thesis presented by Sean Higgins, B.Sc., to The University of St. Andrews in application for the degree of Doctor of Philosophy.

August 1997

"work is the curse of the drinking classes"

Oscar Fingal O'Flahertie Wills Wilde

Declarations

I, Sean Higgins, hereby certify that this thesis, which is approximately fifty thousand words in length, has been written by me, that it is a record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

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"Aspects of Materials Chemistry"	Dr. J.A. Crayston
"Cyclic Voltammetry"	Dr. J.A. Crayston
"Ligand Design"	Prof. R.W. Hay
"Advanced Electrochemistry"	Prof. C.A. Vincent
"Molecular Rearrangements"	Dr. J.C. Walton

List of Abbreviations

acn	Acetonitrile
ADC	Atom Designator Code
bzn	Benzonitrile
CB	Conduction Band
$CDCl_3$	Chloroform-*d*
CE	Chemical step followed by electrochemical reaction
cod	1,5-Cyclooctadiene
CV	Cyclic Voltammetry or Cyclic Voltammogram
δ	Relative to tetramethylsilane
dppp	1,3-Bis(diphenylphosphino)propane
DMF	Dimethylformamide
EC	Electrochemical step followed by chemical reaction
edta	Ethylene diamine tetra-acetic acid
FTIR	Fourier Transform Infra Red
HDTV	High Definition Television
HOMO	Highest Occupied Molecular Orbital
ITO	Indium / tin oxide-coated glass
LDA	Lithium diisopropylamine
LED	Light Emitting Diode
LUMO	Lowest Unoccupied Molecular Orbital
MHz	Megahertz
mm Hg	Millimetres of mercury
MO	Molecular Orbital
m. pt.	Melting point
MS	Mass Spectrum
NBS	*N*-bromosuccinimide

List of Abbreviations (cont.)

nbz	Nitrobenzene
nmp	*N*-methyl-2-pyrollidone
NMR	Nuclear Magnetic Resonance
pc	Propylene carbonate
PC	Personal Computer
py	Pyridine
RE	Reference Electrode
σ	Conductivity
SCE	Saturated Calomel Electrode
VB	Valence Band
TBAT	Tetrabutylammonium tetrafluoroborate
THF	Tetrahydrofuran
TMS	Trimethylsilane
TMSA	(Trimethylsilyl)acetylene
WE	Working Electrode

Abstract

This study is concerned with the synthesis of conjugated polyheterocycles with potential metal binding sites for applications in sensors, catalysis and electronics. The first synthetic approach to polyheterocycles was based on the interfacial polycondensation of a dihydrazide derivative of pyridine with a diacid chloride to produce a precursor polymer. It was shown, however, the starting materials could not be easily prepared in high yield. Model studies confirmed the feasibility of the route but these studies also suggested that the precursor polymers were unlikely to be very soluble. The second precursor route explored began with the preparation of 2,6-diethynylpyridine. The intermolecular Glaser coupling of the ethyne groups afforded the precursor polymer, poly((2,6'-pyridyl)but-1,3-diyne), as a black powder which was insufficiently soluble to allow conversion to the polyheterocycles.

A series of dimers and trimers containing various combinations of 2-furyl, 2-thienyl and 2-pyridyl moieties were prepared using two different coupling procedures that yielded compounds with the required 2,2'-heteroatom arrangement as required for metal binding. Some of these monomers were electropolymerised and the metal binding properties of these polymers was investigated by cyclic voltammetry. In particular, the two trimers: 2,5-di-(2-thienyl) pyridine; and 2,6-di-(2-thienyl) pyridine showed potential metal coordination despite their hydrophobic nature and impermeability towards metal complexes. Evidence was presented to suggest that these polymers are protonated during the electropolymerisation reaction. X-ray analysis of the 2,5-di-(2-thienyl) pyridine showed that only the 2,2'-linked thiophene was coplanar with the pyridine due to a charge transfer interaction. This interaction insures that S and N atoms have a planar *syn* arrangement conducive to metal binding.

Abstract (cont.)

Several oligothiophenes were prepared to investigate methods for enhancing the solubility of polyheterocycles. The knowledge gained from these investigations was used to prepare a series of regiochemically well-defined poly((3-alkyl)thiophenes). The regularity of these polymers was confirmed by NMR analysis. Related monomers were prepared containing the necessary solubilising alkyl groups as well as phenyl groups designed to act as π-acceptor ligands for the low-valent transition metals such as ruthenium(II). The electrochemistry of these novel thiophene monomers is reported.

Chapter One

Introduction

1.1 The Discovery of Conducting Polymers

The field of conducting polymers began in 1972. A Japanese researcher at the Hidenki Shirakawa laboratory in Tokyo, whilst trying to make the well-known black powder polyacetylene, accidentally (or should we say fortunately!), added a thousand times more catalyst than was required. Polyacetylene was made, but this time in a form that was previously unknown[1.1]. Instead of being a black powder, the polymer had a metallic look (like aluminium foil). This new form of polyacetylene showed several orders of magnitude increase in conductivity and hence the field of conducting polymers had begun.

The next major development was reached in 1977 when the two Americans, Alan MacDiarmid and Alan Heeger, while working with Shirakawa at the University of Pennsylvania had the idea of doping (addition of known impurities to gain beneficial effects) the new form of polyacetylene, with iodine[1.2]. This time the polyacetylene resembled gold leaf and was a far better conductor. It had a conductivity of $10^3\ \Omega^{-1}cm^{-1}$ compared to a conductor, copper, that has a conductivity of $10^6\ \Omega^{-1}cm^{-1}$, and an insulator such as glass with a conductivity of $10^{-10}\ \Omega^{-1}cm^{-1}$.

Since these early days of conducting polymers, there have been thousands of different conducting polymers prepared. A major component of this large field are the heterocyclic polymers. The aim of this project is to design heterocyclic conducting polymers and to investigate their metal binding ability. To enable metals to bind

directly to the polymer backbone we require the heterocycles to be arranged in a specific 2,2'-manner, as in 2,2'-bipyridine. In contrast to the pendant ligand systems[1.3], these ligands are directly conjugated with the backbone of the conducting polymer, and hence the polymer may exert greater influence on the redox and magnetic properties of the metal centre. Recent reports of polypyridine[1.4] and poly(2,2'-bipyridine)[1.5] as well as copolymers of pyridine and thiophene[1.6] have appeared, but little is known about their metal binding ability[1.7], although it is known that the simple monomer 2-(2-thienyl) pyridine can co-ordinate to platinum metal[1.8].

In the following sections of this introduction, we will compare some various types of conducting polymers, the methods used to prepare them and explore the mechanism behind their conductivity. We shall also discuss some of the present uses of these polymers and take a brief look into some of the future uses.

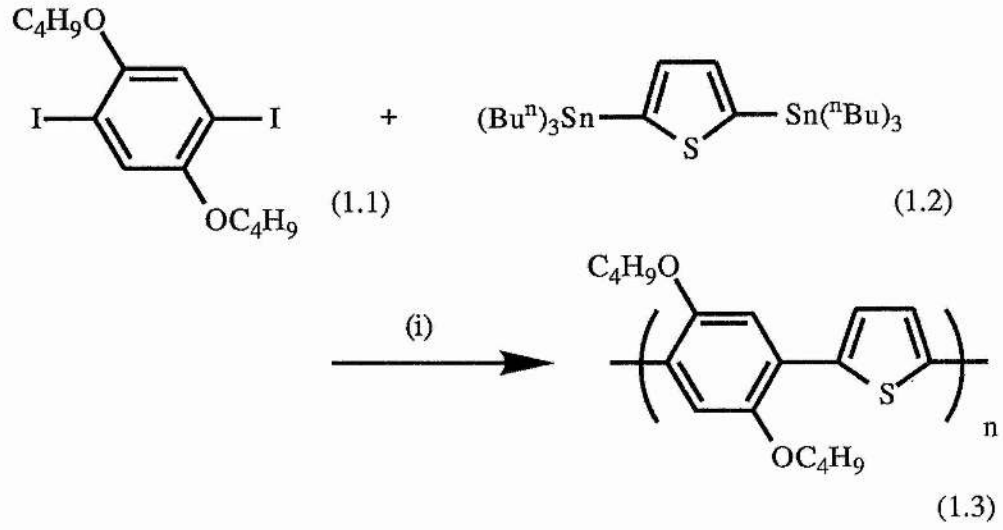
1.2 Methods of Chemically Synthesising Heterocyclic Conducting Polymers

Heterocyclic polymers include a vast range of materials, from the seemingly straightforward and uncomplicated linear polymers prepared using simple heterocyclic monomers to the highly functionalised, cross-linked networks in which the heterocycle has been generated during the polymerisation or network forming reaction. Technically, any macromolecule that contains a repeating heterocycle in the main chain, side chain or terminus is a heterocyclic polymer. The term 'polymer' is generally used to describe a macromolecule that consists of five or more repeating units. Substances that contain a lower degree of polymerisation, i.e. heterocyclic oligomers, have also been reviewed[1.9].

The chemical synthesis of heterocyclic polymers may be divided into three major categories based on their method of synthesis: (a) heterocyclic polymers from heterocyclic monomers; (b) heterocyclic-forming polymerisations; and (c) heterocyclic polymers via polymer modification. These categories constitute the remainder of this section.

(a) Heterocyclic polymers from heterocyclic monomers:- The preparation of polymers from heterocyclic monomers that contain polymerisable functional groups, constitutes the most common method of incorporating heterocycles into polymeric materials. Polymer forming reactions are of two types either condensation reactions or addition reactions. In reactions involving condensation monomers a bond is formed between two monomers with the subsequent elimination of a by-product, usually a small molecule such as water, hydrochloric acid, ammonia or an alcohol. On the other hand, addition monomers, generally contain a site of unsaturation, i.e. a double or triple bond, and the polymerisation occurs by successive single bond formation from one monomer to the next.

There are many examples of classical synthetic procedures which have been adapted for use in polymerisation reactions. These include: Suzuki cross-coupling of arylboronic acid (or esters) and aryl halides under catalysis with palladium[1.10]; Stille type cross-coupling of aryltin reagents with organic electrophiles again catalysed by palladium[1.11]; and Heck type cross-coupling which involves carbon-carbon bond formation between an aryl halide and a vinyl functionallity[1.12]. As an example Scheme I.I outlines a Stille type, palladium catalysed, cross-coupling reaction of 1,4-dibutoxy-2,5-diiodo-benzene (1.1) with 2,5-bis(tributlytin) thiophene (1.2). The polymer, poly[2,5-thiophenediyl(2,5-dibutoxy-1,4-phenylene)] (1.3), was obtained in average yields of 12% after precipitation from acetone. Due to the electroactivity and solubility, polymers of this type have found roles in the areas of novel electroactive and non-linear optically active materials.

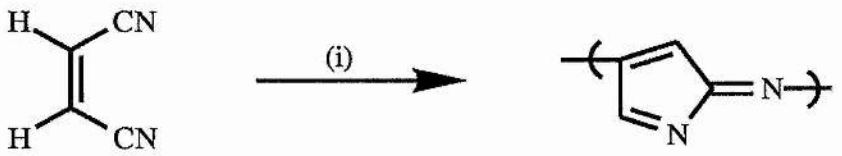


(i) $Pd(PPh_3)_2Cl_2$ / THF.

Scheme I.I

(b) Heterocyclic-forming polymerisations:- This technique generally employs an addition polymerisation reaction involving a monomer that contains two polymerisable groups. Although normally you would expect a cross-linked, insoluble polymer to be formed, under certain conditions an alternating intermolecular-intramolecular chain propagation reaction results in a linear polymer. An example of this so-called cyclopolymerisation can be seen in the reaction of (Z)-2-butenedinitrile (1.4)[1.14] - Scheme I.II.

The reason for this reaction is not known for certain. The best explanation that seems to fit most of the experimental results is that the nonconjugated dienes are associated in their ground state. Intramolecular cyclopolymerisation is thus favoured over intermolecular polymerisation even before attack by a radical, and the overall cyclisation process, from attack by the radical to formation of the propagating cyclic radical, is concerted.



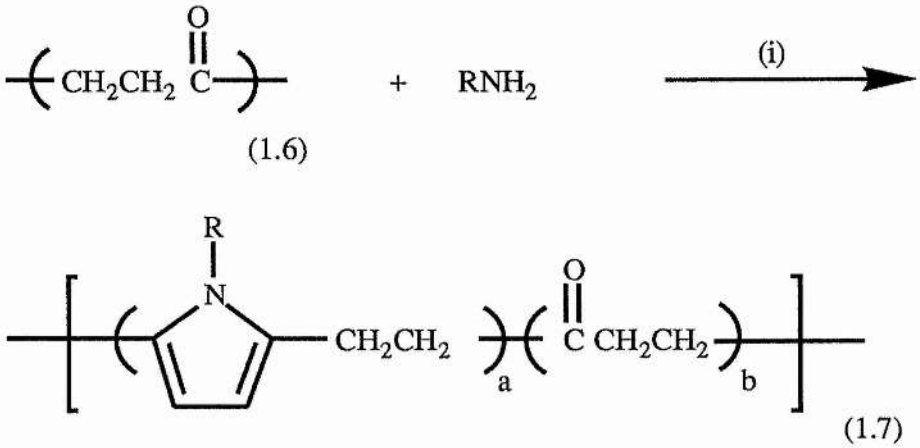
(1.4) (1.5)

(i) $(Bu^tO)_2$ / 160°C

Scheme I.II

(c) Heterocyclic polymers via polymer modification:- This method involves the manipulation of a preformed polymer. The main advantage of preparing a heterocyclic polymer via modification of an existing polymer is that the degree of reaction, and hence the concentration of the heterocycle, can be controlled and varied without altering the degree of polymerisation. This is often a problem in the preparation of heterocyclic polymers from heterocyclic monomers, for example. These monomers often contain functionality that is not compatible with the ensuing addition polymerisation reaction because of reactions leading to chain transfer or even outright inhibition. An example of this type of reaction is the inclusion of a pyrrole heterocycle into the main chain of a polymer[1.15]. This has been readily accomplished by the treatment of an ethylene-carbon monoxide interpolymer (1.6) with a primary amine in the presence of acid - Scheme I.III.

The ratio of $a : b$ is controlled by the size of the R group in the primary amine, the greater the size of R, the greater the conversion of poly(ketone) to pyrrole units. The example where R=heptyl gives a conversion of $a : b = 0.1$ and the polymer formed was very resistant to dissolution or swelling in petrol and oil and hence they are suitable for use as automobile trim mouldings.



(i) Cl_3CCOOH

Scheme I.III

1.3 Methods of Electrochemically Synthesising Heterocyclic Conducting Polymers

Many conducting polymers can in principle be electrochemically synthesised[1.16]. Although the oxidative anodic electropolymerisation of a monomer is the most convenient and most widely used method, cathodic routes have been reported. A method initially reported for the synthesis of poly(*p*-phenylene)[1.17] has been extended for the synthesis of polythiophene[1.18]. This cathodic route involves the electroreduction of the complex (2-bromo-5-thienyl)triphenylnickel bromide in acetonitrile. The major drawback of this method is that the polymer is produced in its neutral insulating form which leads to the rapid electrode passivation and limits the film thickness.

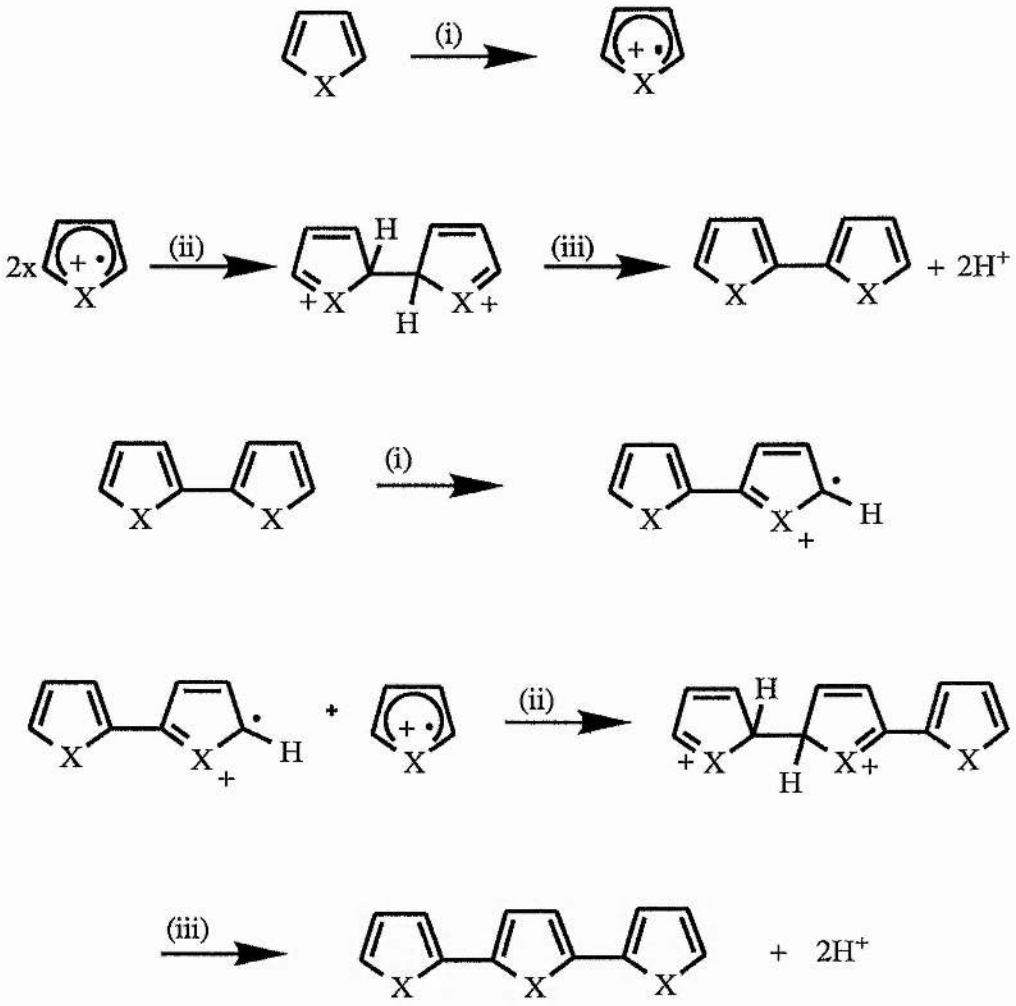
The anodic electropolymerisation method for the synthesis of conducting poly(heterocycles) presents several advantages over other chemical or electrochemical

preparations[1.19]. These include: an absence of catalyst; direct grafting of the doped conducting polymer onto the electrode; easy control of the film thickness by the deposition charge; and the possibility to perform a first *in situ.* characterisation by electrochemical and/or spectroscopic techniques. The main requirements for the electrochemical synthesis of conducting poly(heterocycles) are that the monomer[1.20]: (a) has an oxidation potential which is accessible via a suitable solvent system; (b) will produce a radical cation which reacts more quickly with other monomers to form the polymer than it will with other nucleophiles in the electrolyte solution[1.21]; and (c) produces a polymer with lower oxidation potential than that of the monomer (if the material is to be produced in a state which has a higher conductivity).

The mechanism for the electropolymerisation of a conducting polymer is a unique process. It presents some similarities with the electrodeposition of metals since it proceeds via a nucleation and phase-growth mechanism[1.22]. The major difference lies in the fact that the charged species precursors of the deposited material must be initially produced by the oxidation of the neutral monomer at the anode surface. The consequence of this is that the various electrochemical and chemical follow-up reactions are possible, making the elucidation of the electropolymerisation mechanism a very complex problem.

Most theoretical studies on the electropolymerisation mechanism for poly(heterocycles) have been carried out using pyrrole[1.16, 1.23] as a model compound and it is assumed that all heterocyclic polymerisations proceed by a similar mechanism. By making an analogy to the already known coupling reactions of aromatic compounds[1.24] it is possible to propose a mechanism for the electropolymerisation of heterocyclic monomers[1.25] - Scheme I.IV.

The first step of the electropolymerisation mechanism is the oxidation of the monomer to its radical cation (E). Since the electron transfer reaction is much faster



(i) oxidation to radical cation.

(ii) radical coupling to produce dihydro dimer.

(iii) rearomatisation and loss of two protons.

Scheme I.IV

than the diffusion of the monomer from the bulk solution, it follows that a high concentration of radicals is continuously maintained near the electrode surface. The second step involves the coupling of two radicals to produce a dihydro dimer dication which leads to a dimer after rearomatisation and loss of two protons. This

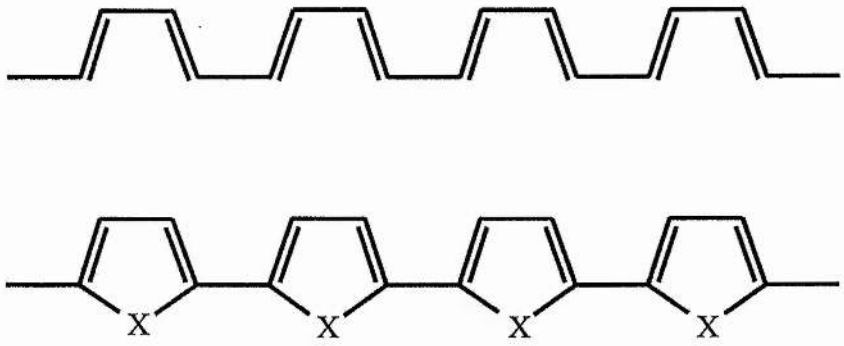
rearomatisation constitutes the driving force of the chemical step (C). Due to the applied potential, the dimer, which is more easily oxidised than the monomer, occurs in its radical form and undergoes a further coupling with monomeric radical. Thus the electropolymerisation proceeds through successive electrochemical and chemical steps according to the general $E(CE)_n$ scheme, until the oligomer becomes insoluble in the electrolytic medium and precipitates on the electrode surface. Note however that this scheme takes no account of the polaron, bipolaron formation within the polymer chain. The oxidation of monomer requires 2 electrons / molecule while the excess of charge corresponds to the reversible oxidation or doping of the polymer, this is further explored in the theory section - Section 1.4.

Although this mechanism seems to explain the electropolymerisation of monomeric heterocycles there are still plenty of unanswered questions[1.19] such as: which step is rate-limiting; the exact role of oligomers in both the initial step and chain propagation; the effect of solvents; concentration of monomers; and other physical conditions.

1.4 Theory Behind the Conductivity of Conducting Polymers

The conductivity of these so called conducting polymers is due to the π-system which extends over a large number of repeating monomer units. This results in low dimensional materials with a high anisotropy of conductivity which is higher along the chain direction.

The simplest example of this type of conducting polymer is polyacetylene and has been the subject of much experimental and theoretical studies[1.26]. Although polyacetylene has a good conductivity, in its doped state, it is environmentally unstable and hence practical application are limited.

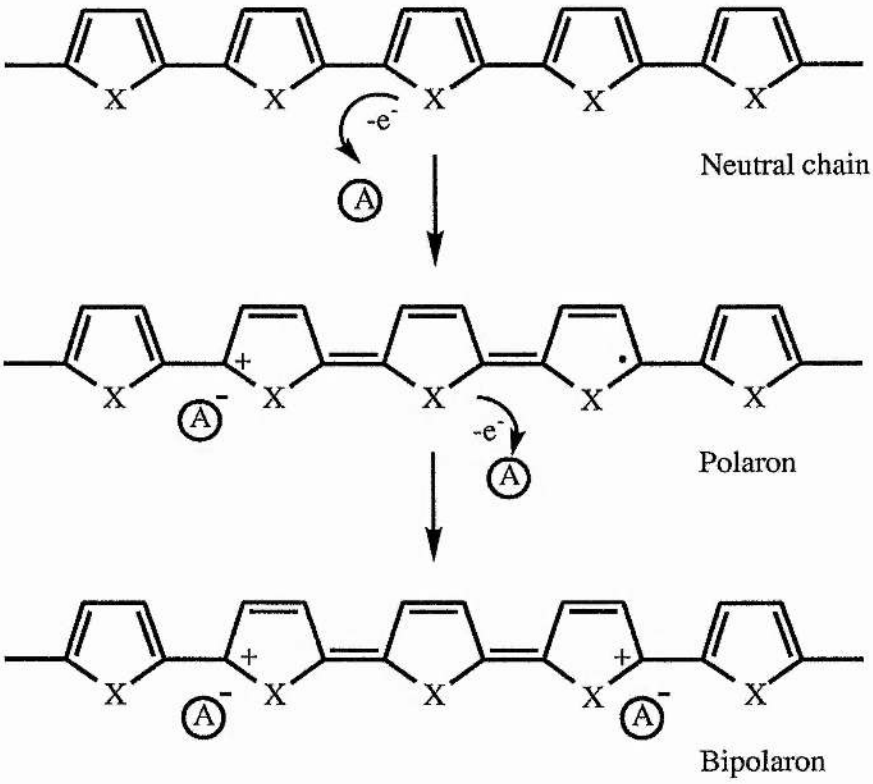


trans-cisoid-$(CH)_n$ compared to poly(heterocycles).

Figure 1.1

Due to this inherent instability of polyacetylene, for the field of conducting polymers to advance, it was essential for this limiting factor to be overcome. If polyacetylene is compared to poly(heterocycles) - Figure 1.1, it can be seen that the poly(heterocycles) can be treated as sp^2p_x carbon chains in which the structure, analogous to that of *trans-cisoid*-$(CH)_n$, is stabilised by the heteroatom. Poly(heterocycles) differ from polyacetylene in many ways: (a) they have good environmental stability, in both the doped and undoped states; (b) their nondegenerate ground states is related to the nonenergetic equivalence of their two limiting mesomeric forms, e.g. aromatic and quinoid; and (c) their structural versatility allows their electrochemical and electronic properties to be manipulated.

The synthesis of polypyrrole in aqueous sulphuric acid was first reported in 1969[1.27], the material produced gave poor mechanical and electrical properties and this work was abandoned. A resurgence of this work came in 1979 when Diaz *et. al.* prepared homogeneous films of polypyrrole by the oxidative electropolymerisation of pyrrole[1.28]. This time the polypyrrole had a high conductivity and was mechanically stable. This electrochemical polymerisation has been extended to include other



Oxidation of a poly(heterocycle) and the creation of polaron and bipolaron states.

Figure 1.2

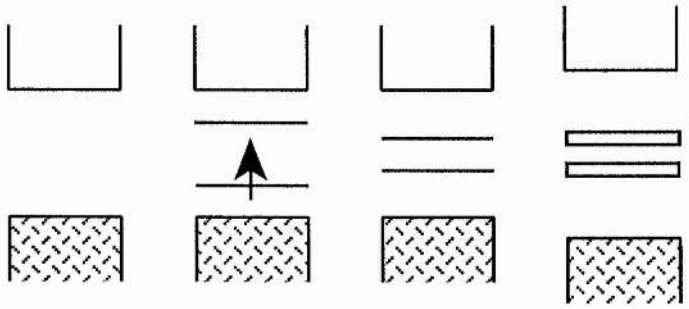
aromatic monomers: thiophene[1.21]; furan[1.29]; indole[1.30]; pyrene[1.31]; benzene[1.29]; and has triggered a renewal of the interest for electrogenerated polyaniline[1.33].

The doping process, in the case of poly(heterocycles), produces polaron and bipolaron sites - Figure 1.2. To begin with, an electron is removed from the π-system of the polymer backbone thereby creating a free radical and a cation. These are coupled to each other by way of a local bond rearrangement, which takes the form of a sequence of quinoid-like rings. This quinoid-like lattice distortion is of higher energy than the remaining benzene-like polymer backbone. As a result of the high energy requirement for creating and separating these defects, the number of quinoid-

like rings which can link together the radical and cation is limited. This combination of a charged site coupled to a free radical via a local distortion is called a polaron and can take the form of a radical cation or a radical anion. Polaron formation results in the production of new localised electronic states in the polymer bandgap - Figure 1.3, with the lower energy states being occupied by single unpaired electrons, consequently a polaron has spin.

With further oxidation another electron can be removed from the polaron or the remaining neural polymer chain. When the electron is removed from the polaron, a dication is formed which consists of two positive charges coupled through a lattice distortion. This spinless defect is termed a bipolaron. Removal of another electron from a different region of the neutral polymer chain, on the other hand, produces a second polaron. Bipolaron formation causes a larger reduction in ionisation energy compared to the formation of two polarons. Therefore bipolaron formation is thermodynamically favoured. Persistent high doping of the polymer creates additional bipolaron states, which, at high doping levels, can overlap to produce continuous bipolaron bands - Figure 1.3. The polymer bandgap is increased during this process and the newly formed bipolaron sites are produced at the expense of the band edge. For conjugated polymers that can be heavily doped, it is theoretically conceivable that the upper and lower bipolaron bands will merge with the conduction and valence bands (CB and VB) to produce partially filled bands and metallic conductivity.

In order for commercial applications of a polymer to be developed, it is imperative that they exhibit good stability and that they are amenable to a variety of processing techniques. Table 1.1 details several representative polymers and lists their conductivities, processing possibilities and their stability. A polymer with 'poor' stability is essentially unstable in its doped state under normal conditions. Conversely, polymers with 'good' stability only experience minor changes even when exposed to abnormal conditions, such as high temperatures, for a long period of time. 'Limited'

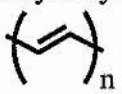
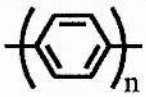
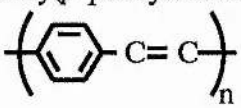
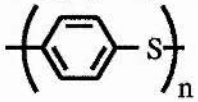
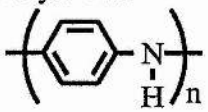
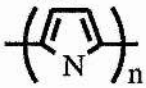
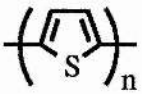


The bandgaps, conduction bands ☐ and valence bands ▨ of the various polymer states.

Figure 1.3

processability means that the polymer can only be processed into unstable forms by specialised methods, such as poly(*p*-phenylene) which is electrochemically prepared in its doped state using catalytic amounts of various salts to promote the polymerisation reaction[1.34]. 'Excellent' processability implies a number of simple conventional methods can be employed, for example polythiophene can be prepared either chemically or electrochemically with a high degree of control of the final product[1.19].

Thus it can be seen that in general, conducting polymers based on polythiophene exhibit the best overall processability and stability with polypyrrole a close second[1.35]. It is also noted that the stability of these poly(heterocycles) can be greatly increased by the addition of an electron donating substituent at C-3 and or C-4. This has the effect of lowering the oxidation potential of the polymer and stabilising its positively charged bipolaron states[1.36]. This addition may also have beneficial effects on the processability of the polymers by making them more soluble. This is explored for polythiophene in Chapter Four.

Polymer	Conductivity (Ω^{-1} cm^{-1})	Stability (doped state)	Processing Possibilities
Polyacetylene 	10^3 to 10^5	poor	limited
Poly(*p*-phenylene) 	10^2 to 10^3	poor	limited
Poly(*p*-phenylenevinylene) 	10 to 10^2	poor	limited
Poly(*p*-phenylenesulphide) 	100 to 500	poor	excellent
Polyaniline 	10 to 200	good	good
Polypyrrole 	10^2 to 10^3	good	good
Polythiophene 	10 to 10^3	good	excellent

Conductivity, stability and processing possibilities of representative conducting polymers.

Table 1.1

1.5 Applications of Conducting Polymers, Past, Present and Future

Nearly two decades have now passed since the discovery of the astonishing increase in the conductivity of polyacetylene, after the addition of a dopant[1.2, 1.37]. At that time, the dream of cheap, light, highly conducting organic polymers seemed close to reality, and hence the race to develop materials for use in batteries, electrochromic displays, microelectronics, sensors, full cells, anti-static coatings and electrode protection began in earnest. Some of these dreams are now becoming a reality.

There have been many publications on the developments and applications of conducting polymers these include reviews by: Chandler and Pletcher[1.38]; Bockris and Miller[1.39]; Meyer[1.40]; Bäuerle[1.41]; Roth[1.42]; and Maiti[1.43]. There are also many specialised papers, these include reviews on: non linear optical activity[1.44]; ESR & ENDOR[1.45]; *in situ.* spectrochemical applications[1.46]; polymer-lithium batteries[1.47]; electrochromic displays[1.48]; molecular electronics[1.49]; field effect transistors[1.50]; metal-containing polymers[1.51]; and uses as lithographic materials[1.52].

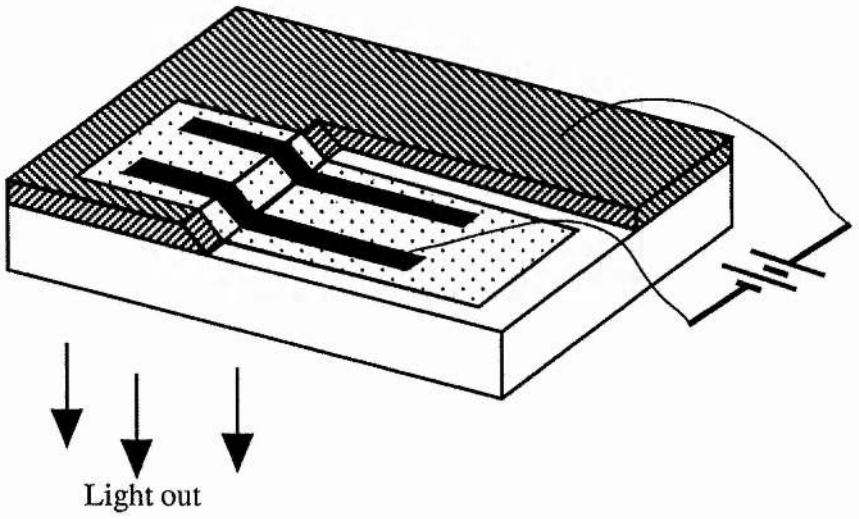
In the remainder of this brief review of the applications of conducting polymers, we shall explore two recent advances that will be bringing the field of conducting polymers out of the laboratory and into our homes over the next few years. These examples are (a) advances in the field of light emitting diodes and (b) advances in the field of electrochromic 'smart windows'.

(a) Advances in the field of light emitting diodes (LED's):- The story of LED's dates back to 1907[1.53]. A LED is a device that radiates light in the visible region in response to an applied voltage. They are commonly seen in alphanumeric displays and as warning or indicator lights, as seen on television sets or stereo systems. These LED's are classically made from inorganic semiconductors, e.g. silicon and gallium

arsenide. There has been much effort over the past thirty years to produce an effective blue LED using inorganic semiconductors. A blue LED or laser diode would be useful in increasing the density of stored information on compact discs. Unfortunately this approach has been unsuccessful due to problems in design fabrication and the rather low luminescence efficiency.

Electroluminescence (the emission of light as the result of injection of charge of opposite sign) of organic materials was first reported for a single crystal of anthracene in 1982[1.54]. Since then there has been enormous advances in the understanding of the processes involved in these organic structures. The blue LED has been developed over the past few years using simple conducting polymers such as poly(*p*-phenylene)[1.55] and have shown comparable efficiency to the best of the inorganic semiconductor LED's. The great advantage of organic electroluminescence devices is the opportunity to tune the colour. This can be done by carefully mixing different subunits to obtain a polymer that will radiate light throughout the visible spectrum[1.56]. For example poly((3-octyl)thiophene), due to its electron rich nature, radiates at the red end of the spectrum (640nm)[1.57] compared with poly(9,9-dihexylfluorene), which emits in the blue end of the spectrum (470nm)[1.58].

Another important breakthrough is the development of mechanically flexible LED's. Alan Heeger's group at Santa Barbara have developed a plastic device based on polyaniline[1.59, 1.60] - Figure 1.4. The luminescence efficiency of these devices is similar to those reported for standard LED's based on indium-tin oxide covered glass. The great advantage of this approach is that polymers are easier to process and fabricate into different shapes. These semiconducting polymer layers can be spin coated from solution and hence the ability to coat large areas. Finally, the mechanical properties of polymers e.g. elasticity, flexibility and toughness are superior to those of conventional brittle semiconductor materials and can lead to new types of devices.



Schematic diagram of the structure of a 'plastic' light emitting diode.

poly(ethylene terephalate) substrate.

polyaniline.

poly(2-methoxy, 5-(2'-ethyl-hexoxy)-1,4-phenylenevinylene).

Calcium electrodes.

Figure 1.4

It can be seen that there is a possibility to produce conducting polymer LED's with a colour range throughout the visible spectrum and which are mechanical flexible. These devices will play an important role in the generation of flat display screens and although probably too late to play a decisive role in the present phase of the race for high definition television (HDTV), will, in the next generation, ultimately lead to all organic television screens. The key issue, however, is whether these new devices are efficient and stable enough to replace the current devices. The major problems with devices of this type are the limited efficiency of the devices, the stability of the light emitting materials and low cycle-lifes[1.61].

(b) Advances in the field of electrochromic 'smart windows':- An

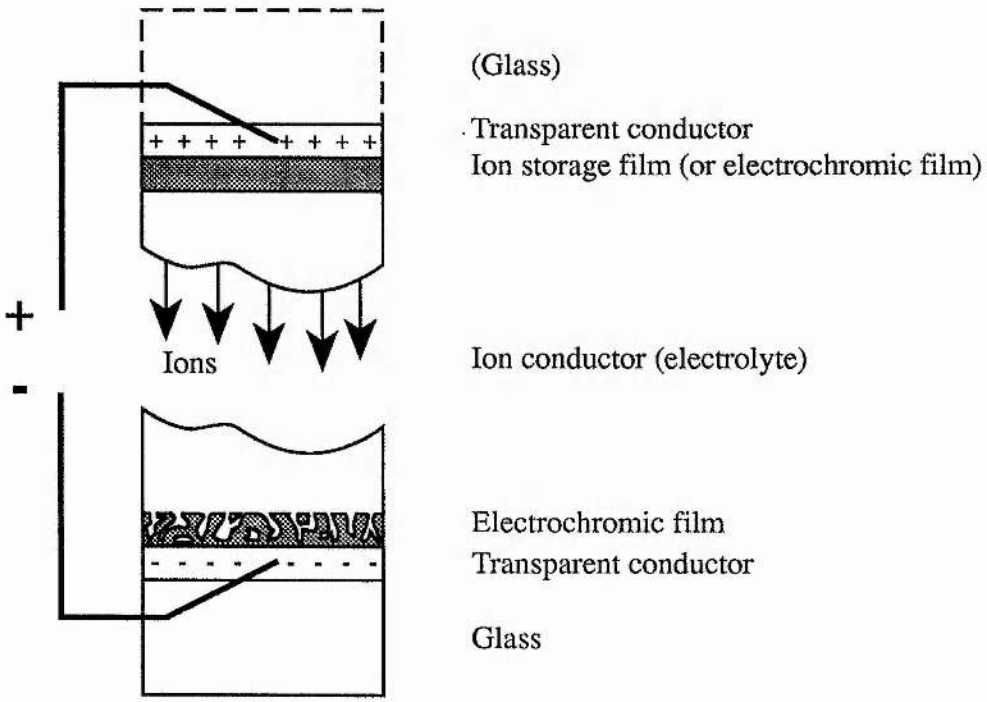
electrochromic device is able to change its optical properties in a reversible and persistent way under the action of a voltage pulse[1.62]. In other words a piece of 'glass' (i.e. window) can be designed that can change from transparent to opaque at the flick of a switch, hence the name 'smart windows'. Numerous inorganic and organic materials have been examined[1.63]. Particularly, properties of inorganic materials such as WO_3, IrO_2 and Prussian Blue are well characterised to the extent of practical uses. All electrochromic devices can be viewed as variations of the same basic design as shown in Figure 1.5.

Several layers are backed by a substrate, which is normally a glass plate, or are positioned in between two substrates. The substrate has a transparent conducting film and a film of the electrochromic material. Then there follows a layer of fast ion conductor or electrolyte which serves as the ion storage layer. The electrochromic and ion storage films are mixed conductors for ions and electrons, whereas the ion conductors ideally should have zero conductivity for electrons. When a voltage is applied between the transparent conductors, ions will be inserted into or extracted from the electrochromic film whose optical properties are thus altered[1.64].

It has been over ten years since the initial reports of electrochromism in conducting polymers. Diaz *et. al.* reported the electrochromic properties for poly-*N*-methylpyrrole in 1981[1.65]. Since then there has been intensive research into the electrochromism of electrochemically polymerised conducting polymers such as polyaniline[1.66], polythiophene[1.67] and mixed inorganic/conducting polymer composites[1.68].

Initially, conducting polymers were used as colourants in electrochromic devices but there are now also being investigated as the conducting material. Conducting polymers will play an important role in the advancement of electrochromic devices. This will be mainly because of their flexible structure, electrical conductivity

and their ability to be made into large, flat and flexible sheets. Almost all conducting polymers which can be electrochemically oxidised or reduced show some form of electrochromism. One major constraint is the voltage range over which these conducting polymers work. For example, in the case of polyaniline[1.69] the electrochromic reaction appears in the potential range of -0.15V to +0.4V (versus Ag/AgCl). Here the transparent yellow colour turns reversibly to blue/green. If the electrode potential exceeds +0.7V, irreversible degradation occurs. Similarly, these organic electrochromic devices suffer from irreversible oxygen bleaching[1.70]. Another disadvantages of using conducting polymers in electrochromic devices are that they often exhibit low cycle-life stability[1.61], as a result of dimensional fluctuation during ion transport processes[1.71]. These problems would have to be overcome if these materials where to become commercially viable.



Basic design of an electrochromic device, indicating transport of positive ions under the action of an electric field.

Figure 1.5

Electrochromic devices will find roles as non-emissive display devices of different sizes. Ever since the discovery of the electrochromic effect in conducting polymers the uses of these devices as replacements for the conventional liquid-crystal based display devices has been discussed[1.72]. They have not yet reached the market place, but the fact that the colour and viewing properties of the conducting polymer devices is far superior to those as reported for standard liquid-crystal based display devices, should allow penetration of the market within the next few years.

Other potential uses of these 'smart windows' will be for providing superior environmental conditions in future buildings. By modulating the luminous and solar energy transmittance of the windows, it will be possible to control the exact spectrum of light entering the building. This will lead to better daylight conditions and greater control of the internal temperature, with a minimum of electric light and a diminished need for air-conditioning. A growing awareness of the imminent dangers of the current levels of energy use, either fossil fuel or nuclear, is bound to advance the research into these new 'smart windows', which should see them in use within the next decade. These 'smart windows' will also find roles in cars, trucks, aeroplanes and perhaps if we can modulate infrared properties, such as thermal emittance, they may play an important role in space technology.

1.6 Aims and Objectives of Research

The original aim of this project was to investigate methods of synthesising conducting polymers with a specific 2,2'-heteroatom arrangement, as in 2,2'-bipyridine. These polymers were to be synthesised using classical electrochemical methods and some the novel chemical procedures that had been recently reported. This 2,2'-heteroatom arrangement should hopefully allow for metal complexation. As the metals would be bound directly to the polymer backbone, they

should exert greater influence on the conducting properties of the polymer.

During the course of these studies we prepared numerous dimers and trimers with the required 2,2'-heteroatom arrangement. These were used as monomers in both electrochemical and chemical polymerisation experiments. The formed polymers were found to be insoluble in most common solvents hence the complexation to metals was not undertaken. There were however, some complexation experiments undertaken using the dimers and trimers.

As this initial work proved difficult, due to the insolubility of the polymers, it was decided to pursue a more productive area that would lead to soluble polymers. The scope of the research was thus extended to include soluble conducting polymers, in particular polythiophene. Firstly, sexithiophene (6T) and quinquethiophene (5T) were prepared to investigate reaction conditions and methods of obtaining solubility. Once the reaction conditions were understood, soluble polythiophenes were prepared and fully characterised. The electrochemistry of these novel, soluble conducting polymer was also fully investigated.

In the following Chapters of the thesis, we firstly deal with the investigations into 'Precursor Routes to Condensed Heterocycles'. Although synthetically unsuccessful this area gave a good insight into the challenges of polymer research. Chapter Three explores the 'Direct Coupling of Heterocycles'. In this section we prepared numerous dimers and trimers containing 2-pyridyl, 2-furyl, and 2-thienyl moieties. These were linked together to give us the required 2,2'-heteroatom arrangement. These dimers and trimers were electrochemically polymerised and their metal binding properties were partially investigated.

Chapters Four and Five covers the areas of 'Synthesis of Polythiophenes' and 'Electrochemistry of Polythiophenes', respectively. In these Chapters the preparation

of some novel soluble oligothiophenes are discussed. These were used as models for investigating methods of obtaining the required solubility. Once the reactions were understood the work was successfully expanded into the synthesis of soluble polythiophenes. All the prepared oligomers and polymers were partially characterised and their electrochemistry was studied.

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1.8 List of Chemicals and Products

1.1 1,4-dibutoxy-2,5-diiodo-benzene.

1.2 2,5-bis(tributlytin) thiophene.

1.3 poly[2,5-thiophenediyl(2,5-dibutoxy-1,4-phenylene)]

1.4 (Z)-2-Butenedinitrile.

1.5 Poly(β-pyrrolenine).

1.6 Ethylene-carbon monoxide interpolymer.

1.7 (*N*-alkyl pyrrole)-ethylene-ketone interpolymer.

Chapter Two

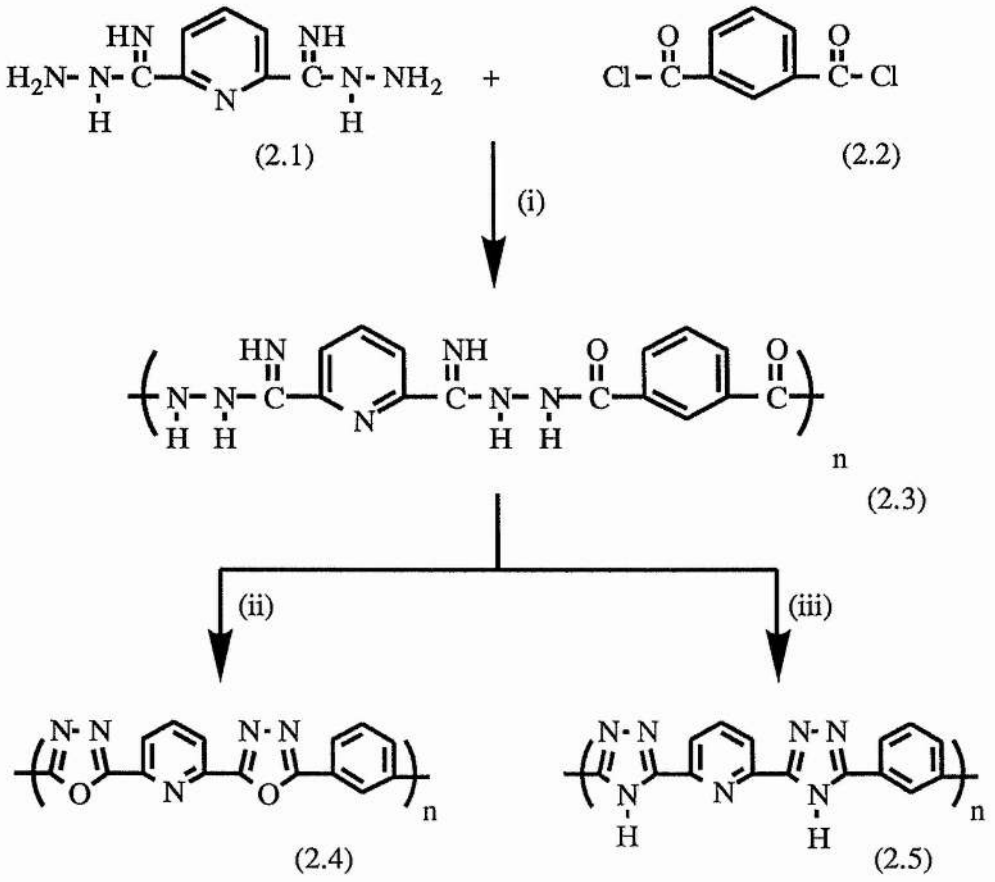
Precursor Routes to Condensed Heterocycles

2.1 Introduction

As discussed in Chapter One, Section 1.2(c), heterocyclic polymers may be prepared by manipulating a preformed or precursor polymer. As we require two heterocycles in our polymers, arranged in the specific 2,2'-manner to enable metal binding, it was decided to attempt the preparation of polymers containing only one heterocycle. These precursor polymers should be prepared so as the second heterocycle can be easily formed after the initial polymerisation reaction. This method is explored for the preparation of a pyridine-furan heterocyclic polymer and a pyridine-thiophene heterocyclic polymer.

2.2 Pyridine-Furan Heterocycles from Poly-*N*-acylhydrazine

Hergenrother[2.1] in 1970 reported the synthesis of poly-1,3,4-oxadiazole (2.4) and poly-1,2,4-triazole (2.5) from precursor poly-*N*-acylhydrazine (2.3) - Scheme II:I. A great advantage of the precursor polymer (2.3) is that it is soluble and hence processable into thin films prior to conversion to poly-1,3,4-oxadiazoles (2.4) or poly-1,2,4-triazoles (2.5), which are insoluble in all solvents tried. As these polymers have the required 1,4-heteroatom arrangement they showed potential as a starting point for this work.



(i) Interfacial polycondensation. CH_2Cl_2 / H_2O.

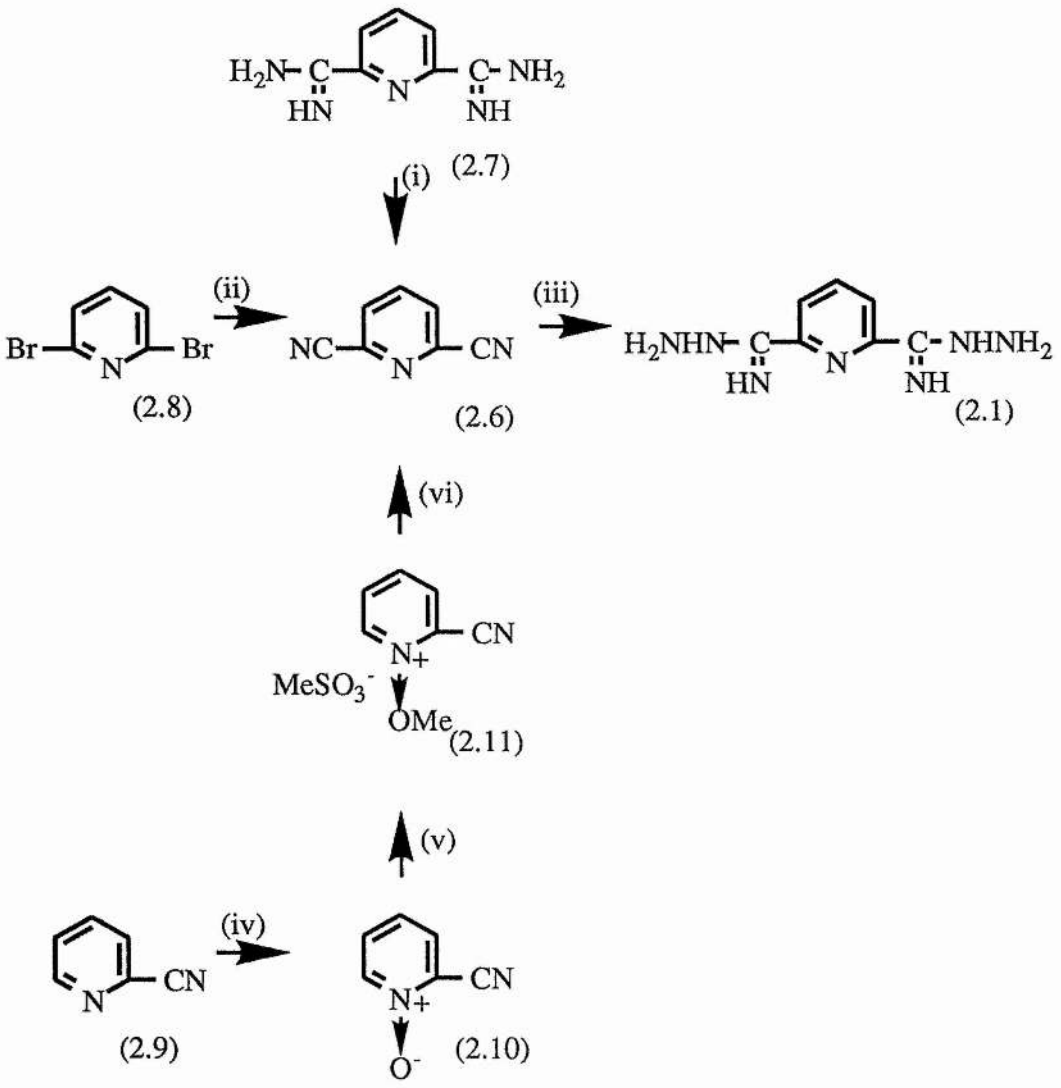
(ii) $-NH_3$.

(iii) $-H_2O$.

Scheme II.I

2.2.1 Synthesis of 2,6-Dicyanopyridine

2,6-Dicyanopyridine (2.6) was required as a starting material for the synthesis of the precursor monomer 2,6-pyridinediyldihydrazidine[2.2] (2.1) - Scheme II:II. A commercial source of 2,6-dicyanopyridine (2.6) could not be found, thus preparation



(i) P_2O_5 or $POCl_3$ or chlorosulphonyl isocyanate.

(ii) CuCN / DMF / reflux.

(iii) Hydrazine hydrate / EtOH / 50°C.

(iv) H_2O_2 / acetic acid / reflux.

(v) Me_2SO_4 / EtOH / H_2O.

(vi) KCN / H_2O.

Scheme II;II

by the dehydration of pyridine-2,6-dicarboxamide (2.7) seemed to be a logical step. The dehydration of pyridine-2,6-dicarboxamide (2.7) has been reported using phosphorus pentoxide[2.3], phosphorus oxychloride[2.4] and chlorosulphonyl isocyanate[2.5]. Attempted preparation via these three steps gave poor yields, an intractable oil or unreacted starting material. Similar low yields, for these methods, have been reported by two other groups[2.6, 2.7]. Barks and Brookes[2.6] proposed an improved method using 1,1,2,2-tetrachloroethane as a mediating solvent and phosphorus oxychloride as the dehydrating agent. The authors of this method reported yields of the order of 50%, the oil obtained proved very difficult to abstract and in our experiments we could only achieve yields less than 10%.

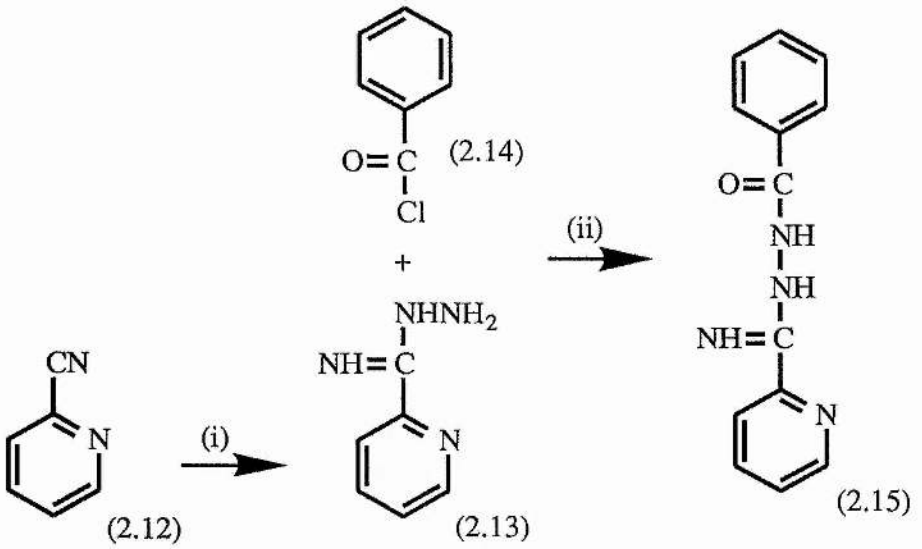
Due to the difficulties with these various methods of dehydration, other methods of preparing 2,6-dicyanopyridine (2.6) were sought from the literature. Two further methods were found. The first of these dates to the work of Tani[2.8] in 1959. This method involves the preparation of the 1-methoxy-2-cyanopyridinium methylsulphate (2.11) from 2-cyanopyridine *N*-oxide (2.10). The 1-methoxy-2-cyanopyridinium methylsulphate (2.11) is then cyanated using potassium cyanide - Scheme II:II. After extraction and chromatography a yield of 84% was claimed. We were only ever able to extract a few percent. Another method is the one reported in 1973, by Pearse & Wisowaty[2.7]. This method involved the cyanation of 2,6-dibromopyridine (2.8), with copper(I) cyanide - Scheme II:II. Although this method was more successful, we were still unable to obtain yields in excess of 10%.

2.2.2 Model Studies

The initial Hergenrother[2.1] paper called for the conversion of 2,6-dicyanopyridine (2.6) to the dihydrazidine derivative, it was therefore decided to attempt the conversion of 2-cyanopyridine (2.12) to test the reaction conditions

reported for the 2,6-dicyanopyridine (2.6). The simple reaction - Scheme II:III, involved the addition of an ethanolic solution of 2-cyanopyridine (2.12) to a solution of hydrazine hydrate[2.9]. The reaction was complete once the temperature had returned to room temperature. Following a standard organic extraction and recrystallisation from toluene, a 91.7% yield of orange crystals was obtained.

As the preparation of the model compound 2-pyridyl hydrazidine (2.13) was a success it was decided to attempt the interfacial condensation reaction with benzoyl chloride - Scheme II:III. This reaction involved the boundary reaction of a solution of 2-pyridyl hydrazidine (2.13) in water with a solution of benzoyl chloride (2.14) in dichloromethane[2.10]. The instantaneous reaction produced a creamy white solid at the solvent interface. The solid obtained was insoluble in all solvents tried. Elemental analysis of the dried solid confirmed the structure of *N*-benzoyl-(2-pyridyl) hydrazidine (2.15) in an acceptable yield of 82.5%.



(i) Hydrazine hydrate / EtOH.

(ii) Interfacial condensation. CH_2Cl_2 / H_2O.

Scheme II:III

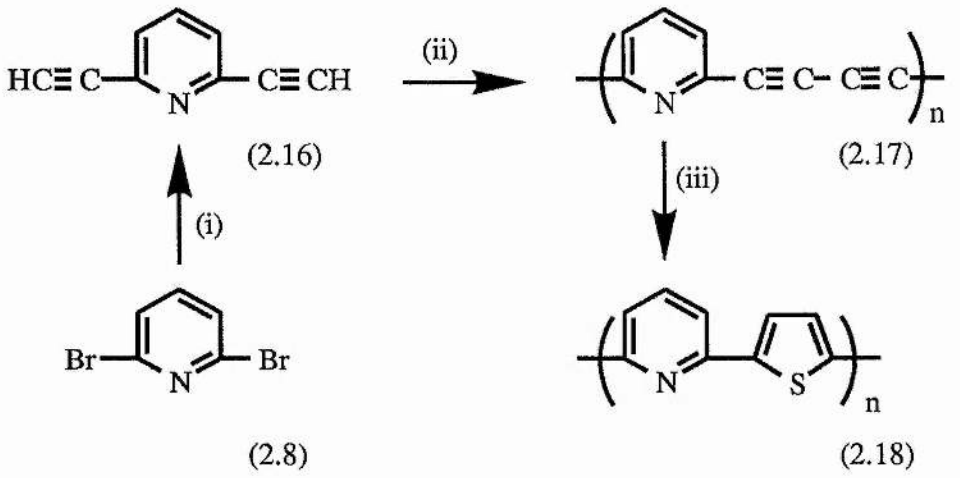
With hindsight it seems that this reaction is more complicated than first thought. Under the proposed reaction scheme an excess of HCl will be produced. It is conceivable that ammonium salts of the assumed product *N*-benzoyl-(2-pyridyl) hydrazidine (2.15) or the starting material 2-pyridyl hydrazidine (2.13) may be formed. The ammonium salt formation is due to protonation, but it is difficult to say which nitrogen would be protonated due to the resonance structure of the hydrazidines. Further investigations would therefore be necessary to elude the exact reaction scheme, for example using base to control the acidity of the reaction mixture.

2.2.3 Conclusions

Although the model compounds showed the preparation of the precursor poly-*N*-acylhydrazines (2.3) may be possible, we were unable to obtain the starting material 2,6-dicyanopyridine (2.6) in sufficient yield. Furthermore, the polymers derived from these materials were likely to be extremely insoluble. It was thus decided to abandon this area of research and pursue a more productive synthetic strategy.

2.3 Pyridine-Thiophene Heterocycles from Poly(but-1,3-diynes)

It has been shown[2.11, 2.12] that in the presence of a cupric catalyst, ethylene groups can be oxidatively coupled to give a but-1,3-diyne system, the so-called Glaser reaction. The but-1,3-diyne can react with sodium sulphide to give a thiophene group[2.13]. Similar work in this area has been carried out by Carpita *et. al.*[2.14]. Their work, from 1985 on the synthesis of π-excessive heteropolyaromatic compounds, showed that this reaction scheme worked for the synthesis of 2,2':5',2''-terthiophene and 2,5-di-(2-furyl) thiophene - see Chapter Three. Due to the success of the work of the Carpita group, it was decided to expand this work and try and oxidatively couple



(i) a) TMSA / (Pd^0/Cu^I cat) / ($^iPr)_2NH$. b) MeOH / KOH.

(ii) O_2 / CuCl / pyridine.

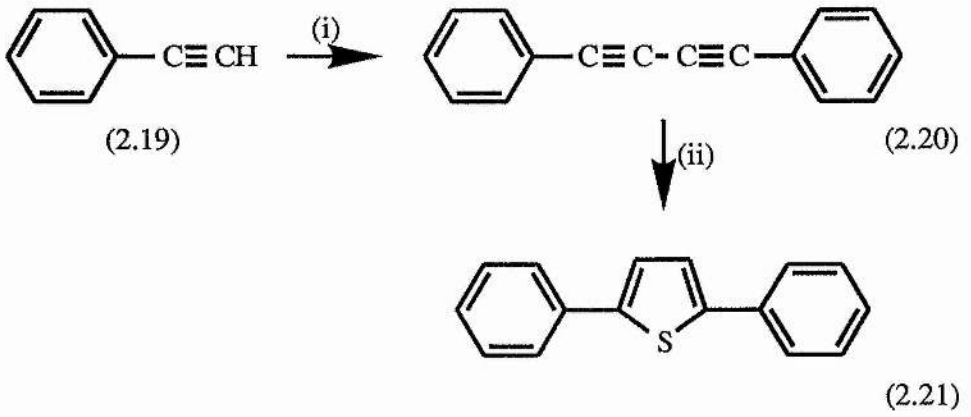
(iii) $Na_2S.9H_2O$ / MeOH / reflux.

Scheme II:IV

2,6-diethynylpyridine (2.16) to give the precursor polymer, poly((2,6'-pyridyl)but-1,3-diyne) (2.17). By reacting this precursor polymer with sodium sulphide in refluxing methanol we should therefore obtain a polymer with the required 1,4-heteroatom arrangement, poly(2-(2'-thienyl)pyridine) (2.18) - Scheme II:IV.

2.3.1 Synthesis of 2,5-Diphenylthiophene as a Model Compound

Before attempting the preparation of 2,6-diethynylpyridine (2.16), it was decided to make a model compound, 2,5-diphenylthiophene (2.21), to test the feasibility of the reaction mechanism and to gain some information about reaction conditions - Scheme II:V.



(2.19) (2.20) (2.21)

(i) O_2 / CuCl / pyridine.

(ii) $Na_2S.9H_2O$ / MeOH / reflux.

Scheme II.V

The Glaser reaction worked particularly well to yield 96% of 1,4-diphenyl-but-1,3-diyne (2.20) as brown needles upon recrystallisation from 40-60 petrol. The addition of sodium sulphide was carried out by refluxing a methanol solution of the 1,4-diphenyl-but-1,3-diyne (2.20) with an excess of sodium sulphide nonahydrate overnight. The mixture was then evaporated to dryness and the resulting solid was washed with water to remove any excess sodium sulphide. The resulting orange solid was dried under vacuum. Recrystallisation of this solid from ethanol gave a quantitative yield of 2,5-diphenylthiophene (2.21) as orange flakes with a metallic lustre. Both these model compounds were characterised by nuclear magnetic resonance spectroscopy. Figure 2.1 shows the ^{13}C NMR spectra for the two model compounds.

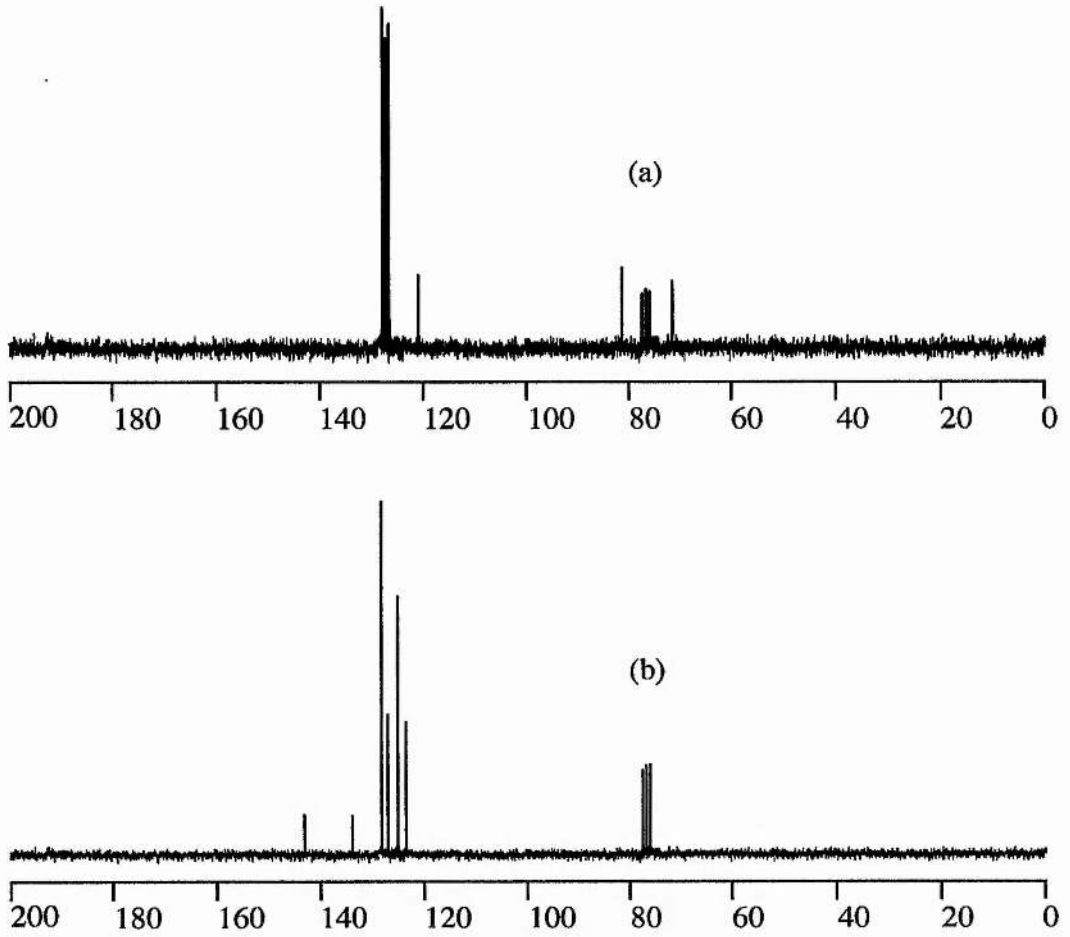
Both compounds have six aromatic resonances due to the symmetric nature of the molecules. There is complete conversion of the 1,4-diphenyl-but-1,3-diyne (2.20) to the 2,5-diphenylthiophene (2.21) as noted by the complete disappearance of the

two ethynylene peaks at 81.6ppm and 74.1ppm - Figure 2.1. As both these model compounds were made easily and with high yield it was decided to continue with this approach and attempt to prepare 2,6-diethynylpyridine (2.16) in the first step towards the precursor polymer (2.17).

2.3.2 Synthesis of 2,6-Diethynylpyridine

The synthesis of terminal aryl acetylenes classically involves the manipulation of preformed two-carbon units[2.15], in particular the Vilsmeier reaction[2.16], the dehydrohalogenation of β,β-dihalo olefins[2.17] and the halogenation-dehydrohalogenation of vinyl aromatics[2.18]. The latter of these has been applied by Hay[2.19] for the preparation of diethynylbenzene from divinylbenzene via bromination followed by dehydrohalogenation using potassium t-butoxide. Although the yield was low this mechanism showed potential. Unfortunately, the starting divinylpyridine is not commercially available and therefore another route was sought.

An alternative method involves the addition of a protected ethynyl moiety directly onto the aromatic ring. These include a modified Stephens-Castro[2.20] method, which involves the coupling between arylcopper reagents and (iodoethynyl)-trimethylsilane at low temperatures. This method is limited by the necessity to form organocopper reagents. Hagihara *et. al.*[2.21] in 1980 reported a palladium(0) and copper(I) catalytic system that couples (trimethylsilyl)acetylene (TMSA)[2.22] to aryl halides. This yields a stable, easily handled TMS-protected ethynyl aromatic as an intermediate. Mild base deprotects the intermediate by removal of TMS. Vollhardt[2.23] in 1986 showed that this method could be used to replace multiple halogens on the same aromatic ring. It was therefore decided to prepare the monomer 2,6-diethynylpyridine (2.16) by the TMS-protected intermediate.



^{13}C NMR (50MHz) $\delta(CDCl_3)$ spectra for (a) 1,4-diphenyl-but-1,3-diyne (2.20) and (b) 2,5-diphenylthiophene (2.21).

Figure 2.1

The TMSA was prepared by the method of Holmes and Sporikou[2.22]. This complicated procedure involves the reaction of a simple Grignard with ethylene gas in a solution of THF at low temperatures. Once the ethylene Grignard had formed a solution of chlorotrimethylsilane was added, again at low temperature. The protected TMSA was then collected by careful distillation, separation and drying, to give an acceptable yield (79.8%) of a colourless liquid.

The synthesis of 2,6-diethynylpyridine (2.16) involves the reaction of 2,6-dibromopyridine (2.8), TMSA and the palladium/cupric catalyst mixture. The colourful reaction proceeded from light purple, through brown to a deep blood red. After several processing steps to remove the catalyst, hydrolysis to remove the TMS protection group and recrystallisation from hexane the target compound, 2,6-diethynylpyridine (2.16), was collected as colourless crystals in a yield of 52.5%.

2.3.3 Synthesis of Poly((2,6'-pyridyl)but-1,3-diyne)

In 1989, the Italian group E. Cernia *et. al.*[2.24], reported the synthesis of poly(ethynylene(2,5-thiophenediyl)ethynylene). This procedure involves the cuprous catalysed oxidative coupling reaction as used by Hay[2.19] and discussed earlier in the preparation of our model compound 1,4-diphenyl-but-1,3-diyne (2.20). This method was again successfully used for the synthesis of poly((2,6'-pyridyl)but-1,3-diyne) (2.17), as described in Scheme II.IV. The polymer precipitates from the reaction solution after the oxidative coupling of 2,6-diethynylpyridine (2.16) with oxygen and a catalytic amount of cuprous chloride in pyridine as a black powder. The structure of the polymer was confirmed by elemental analysis.

2.3.4 Attempted Synthesis of Poly(2-(2'-thienyl)pyridine)

The synthesis of poly(2-(2'-thienyl)pyridine) (2.18) by the addition of sodium sulphide was not carried out as the precursor polymer was insoluble in all solvents tried and hence the reaction was unable to proceed as laid out in Scheme II:IV. As the polymer was later obtained by the direct coupling method - Chapter Three, it was decided not to continue with this approach. The synthesis by this technique has been shown to be effective in the preparation of poly((*N*-phenyl-2,5-pyrrolediyl)(β-hexyl-

2,5-thiophenediyl)) as described by Rutherford and Stille[2.25]. They prepared the chloroform-soluble polymer by the addition of aniline to the soluble precursor polymer, poly(ethynylene(3-hexyl-2,5-thiophenediyl)ethynylene). Their paper also discusses the increase in solubility of poly(ethynylene(2,5-thiophenediyl)ethynylenes) by the addition of various alkyl groups, at the β-positions on the aromatic portions of the polymer. They report that the brown polymer, poly(ethynylene(3-methyl-2,5-thiophenediyl)ethynylene) is only partially soluble in hot nitrobenzene and hot chlorobenzene, whereas the purple polymer, poly(ethynylene(3-hexyl-2,5-thiophenediyl)ethynylene) is completely soluble. It was also found to be partially soluble in tetrachloromethane. Therefore, if we made our precursor polymer soluble, by the addition of an alkyl chain, this method would probably be successful.

2.3.5 Conclusions

This area of research showed great potential to prepare conducting polymers with the required 2,2'-heteroatom configuration. The initial approach, using the Hergenrother[2.1, 2.2] method, unfortunately had to be abandoned as we were unable to prepare the starting material 2,6-dicyanopyridine (2.6) in sufficient quantities.

The strategy of preparing a but-1,3-diyne system could be extended to include any heterocycle. By using a substituted monomer e.g. 3-alkyl-2,6-diethynylpyridine, we should hopefully obtain a soluble precursor polymer, and hence be able to undergo the addition of sodium suphide reaction to achieve the required polymer. However, at this time we became aware of the superior newly developed routes to soluble, processable polythiophenes as prepared and characterised in Chapter Four.

2.4 Experimental

(2.6) Attempted synthesis of 2,6-dicyanopyridine, using phosphorus pentoxide

In a 250ml, round bottomed flask equipped for distillation at 30mm Hg, was placed pyridine-2,6-dicarboxamide (16.5g, 0.1moles) and phosphorus pentoxide (35.5g, 0.25moles). Maintaining the pressure at 30mm Hg the flask was immersed in an oil bath and the temperature was raised to 200°C, however nothing distilled over. The residual solid was extracted with 100ml dichloromethane. Evaporation of the solvent left a pink solid. FTIR of this solid showed no nitrile stretch in the region of 2260-2200cm^{-1}.

(2.6) Attempted synthesis of 2,6-dicyanopyridine, using phosphorus oxychloride

In a 100ml, round bottomed flask equipped with a reflux condenser, was placed pyridine-2,6-dicarboxamide (16.5g, 0.1moles) and 25ml phosphorus oxychloride. The reaction was heated to reflux, where upon white acidic fumes were given off. The reaction was maintained at reflux for three hours. The excess phosphorus oxychloride was distilled off leaving a pink solid which was made alkali by the addition of 100ml saturated potassium carbonate solution. This was then extracted with 2x100ml dichloromethane. The organic layer was washed with 3x100ml water, dried and concentrated. FTIR of the dark brown solid showed no nitrile stretch in the region of 2260-2200cm^{-1}.

(2.6) Attempted synthesis of 2,6-dicyanopyridine, using chlorosulphonyl isocyanate

In a 100ml, three necked flask equipped with a stirrer, a reflux condenser and a dropping funnel, was placed pyridine-2,6-dicarboxamide (1.65g, 0.01moles), triethylamine (4.04g, 0.04moles) and 10ml dichloromethane. To the stirred solution, at 0°C was added dropwise a solution of chlorosulphonyl isocyanate (3.53g, 0.025moles) in 10ml dichloromethane. Addition was complete in ten minutes, and the reaction was left to stir for seven hours at room temperature. The brown solid was removed and the filtrate washed with 3x25ml water, dried and concentrated. ^{1}H NMR of the resulting oil showed no aromatic peaks and FTIR showed no nitrile stretch in the region 2260-2200cm^{-1}.

(2.6) Synthesis of 2,6-dicyanopyridine, using phosphorus oxychloride and 1,1,2,2-tetrachloroethane as a mediating solvent

In a 500ml, three necked flask equipped with a mechanical stirrer, a dropping funnel and a reflux condenser was placed finely powdered pyridine-2,6-dicarboxamide (5g, 0.03moles) and 200ml of 1,1,2,2-tetrachloromethane. The vigorously stirred suspension was heated to reflux while phosphorous oxychloride (25g, 0.16moles) was added dropwise. The mixture was stirred at reflux for one hour. The green solid was removed by filtration and the solvents removed under vacuum, below 60°C. The residue solidified on cooling and was dissolved in 200ml dichloromethane, washed with 3x75ml saturated sodium carbonate solution, 2x100ml of water, dried and concentrated. The resulting solid was recrystallised from ethanol to yield the title compound as colourless crystals, weight 0.28g (7.2%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 8.2-8.0 (m, AB_2 pattern). ^{13}C NMR (50MHz) $\delta(CDCl_3)$

138.926, 135.064, 131.619, 115.705.

(2.6) Synthesis of 2,6-dicyanopyridine, via cyanation of 1-methoxy-2-cyanopyridinium methylsulphate

In a 250ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser was placed 2-cyanopyridine *N*-oxide (6g, 0.05moles) and dimethyl sulphate (7g, 0.055moles). The mixture was heated at reflux for one hour and then left to stir overnight. To this was added 80ml of ethanol and 20ml of water, followed by the dropwise addition of a solution of potassium cyanide (3.5g, 0.055moles) in 20ml of water. The addition was complete in thirty minutes and the mixture was then heated at reflux for one hour. The cooled solution was extracted with 2x50ml, dried and concentrated to 1ml. This was chromatographed onto Al_2O_3 using ethanol as the elutant. ^1H NMR studies of the factions showed mainly the starting compound, 2-cyanopyridine *N*-oxide. A few colourless crystals, 0.45g (6.9%), of the title product were collected. ^1H NMR (200MHz) $\delta(CDCl_3)$ 8.34-7.90 (m, AB_2 pattern).

(2.6) Synthesis of 2,6-dicyanopyridine, cyanation using copper(I) cyanide

In a 250ml, three necked flask equipped with a mechanical stirrer and a reflux condenser, was placed 2,6-dibromopyridine (9.48, 0.04moles), copper(I) cyanide (8.0g, 0.09moles) and 50ml DMF. The stirrer was started and the dark brown mixture was refluxed for three and a half hours. Whilst still hot the mixture was poured onto 400ml of water. The brown suspension was removed and retained for later. The filtrate was made alkaline with dilute aqueous ammonia solution and extracted with 2x100ml dichloromethane. The brown solid was dissolved in 1:1

ammonia:water solution and filtered. The dark blue filtrate was extracted with 3x100ml dichloromethane. The combined organic layers were washed with 3x200ml water, until neutral, dried and concentrated to yield a light brown liquid. Upon cooling the title compound was collected as colourless crystals, weight 0.59g (9.7%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 8.14-7.92 (m, AB_2 pattern). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 139.165, 132.228, 131.719, 115.503.

(2.10) Synthesis of 2-cyanopyridine *N*-oxide

In a 500ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser was placed 2-cyanopyridine (5.2g, 0.05moles) and 100ml acetic acid. To the stirred solution was added hydrogen peroxide (100vols, 50g). The reaction was refluxed for one hour and a further quantity of hydrogen peroxide (100vols, 35g) was added. The resulting mixture was stirred at reflux for a further two hours. The solvents were removed under vacuum. The solid obtained was recrystallised from diethylether to yield the title compound as yellow needles, m. pt. 117-118°C, weight 4.6g (76.7%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 8.31 (d of t, 1H), 7.72 (d of d, 1H), 7.54 (t of d, 1H), 7.37 (t of d, 1H). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 140.254, 132.420, 130.572, 125.632, 123.572, 112.876. FTIR 2244cm^{-1} υ(CN), 1266cm^{-1} υ(NO). MS m/z (relative intensity) 120 (M+ 76), 104 (11), 93 (4), 78 (13). Anal. calc. for $C_6H_4N_2O$: C (60.00), H (3.36), N (23.32). Found: C (59.08), H (3.18), N (23.36).

(2.13) Synthesis of 2-pyridyl hydrazidine

In a 250ml, three necked flask equipped with a stirrer, a thermometer, a reflux condenser and a dropping funnel was placed 2-cyanopyridine (5.2g, 0.05moles) and

9ml of ethanol. To this was added 25ml hydrazine hydrate (55%). The reaction was warmed to 40°C and stirred for two hours. The cooled mixture was poured onto 30ml of water, extracted with 4x50ml dichloromethane, dried and concentrated. The resulting yellow solid was recrystallised from toluene to yield the title compound as orange crystals, m. pt. 46°C, weight 6.2g (91.7%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 8.4 (d, 1H), 8.0 (d, 1H), 7.6 (t, 1H), 7.2 (t, 1H). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 150.851, 148.532, 147.889, 136.324, 123.711, 119.680. MS m/z (relative intensity) 136 (M+ 100), 105 (92), 78 (61).

(2.15) Synthesis of *N*-benzoyl-(2-pyridyl) hydrazidine

In a 1L, conical flask was placed 2-pyridyl hydrazidine (5.44g, 0.04moles) and 500ml water. To the stirred solution at room temperature, was added a solution of benzoyl chloride (5.62g, 0.04moles) in 150ml dichloromethane over a ten minute period. The mixture was stirred for a further thirty minutes. The creamy white precipitate was collected, washed with 50ml water followed by 50ml dichloromethane and dried under vacuum. The title compound was thus collected, m. pt. 209°C, weight 7.92g (82.5%). MS m/z (relative intensity) 240 (M+ 31), 223 (36), 105 (100), 77 (42). Anal. calc. for $C_{13}H_{12}N_4O$: C (64.99), H (5.03), N (23.32). Found: C (64.29), H (4.60), N (23.15).

Synthesis of (trimethylsilyl)acetylene

In a 1L, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed dry magnesium turnings (24g, 1mole), a single crystal of iodine and 150ml THF. The mixture was heated to reflux and the heat removed. A solution of 1-chlorobutane (92.5g, 1mole) in 100ml of THF

was placed in the dropping funnel. 25ml of this solution was run into the reaction flask. Once the reaction had started (ether boiling and turbid colour) a further 250ml of THF was added to the reaction flask. The remainder of the 1-chlorobutane solution was added dropwise maintaining gentle reflux. In a second 2L, three necked flask equipped with a mechanical stirrer, a dropping funnel, a reflux condenser and an inlet pipe for the acetylene gas, was placed 500ml THF. Acetylene was bubbled through the mixture at a rate of four bubbles per second. The reaction flask was cooled in an acetone/cardice bath and the hot Grignard was added dropwise maintaining the temperature below 10°C. Once all the Grignard was added the acetylene was continued for thirty minutes. A solution of chlorotrimethylsilane (108.5g, 1mole) in 100ml THF was slowly added, over a period of twenty minutes, again maintaining the temperature below 10°C. The resulting adduct was then refluxed for one hour. The condenser was arranged for downward distillation and the organic layer collected, washed with 10x300ml water (until constant volume) and dried. Distillation yielded the title product at 52°C, weight 78.4g (79.8%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 2.35 (s, 1H), 0.17 (s, 9H). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 93.545, 90.100, 0.172.

(2.16) Synthesis of 2,6-diethynylpyridine

In a 250ml, three necked flask was placed 2,6-dibromopyridine (15g, 0.063moles), 75ml diisopropylamine and the catalyst mixture - [palladium(II) chloride (0.42g, 0.0024moles), triphenylphosphine (1.26g, 0.0048moles) and cupric acetate (0.47g, 0.0024moles)]. The light purple solution was stirred at room temperature and trimethylsilylacetylene (15.4g, 0.158moles) was added over a twenty minute period. The brown solution was heated to reflux, rapidly changing to a blood red colour with the formation of a heavy precipitate. After two hours refluxing the solution was allowed to cool and the precipitated diisopropylamine hydrobromide salts were removed. The solvent was removed at reduced pressure, leaving a black oil. This was

dissolved in 200ml methanol and a solution of potassium hydroxide (0.01g, 0.002moles) in 1ml water was added and left to stir for three hours. The resulting mixture was poured onto 200ml water and extracted with 3x75ml dichloromethane. Solvents were removed at reduced pressure at room temperature, to leave a brown solid. Recrystallisation from hexane yielded the title product as colourless crystals, weight 4.2g (52.5%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 7.7-7.4 (m, 3H), 3.15 (s, 2H). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 143.156, 137.050, 127.579, 82.5492, 78.2526. MS m/z (relative intensity) 127 (M+ 100), 100 (22), 87 (3), 74 (26).

(2.17) Synthesis of poly((2,6'-pyridyl)but-1,3-diyne)

In a 250ml, three necked flask equipped with an inlet for oxygen was placed 2,6-diethynylpyridine (2.2g, 0.017moles) and copper(I) chloride (0.1g, 0.01moles) in 50ml pyridine. Oxygen (5 bubbles per second) was bubbled through the green stirred solution. After thirty minutes a black precipitate started to form. After a further two hours the filtrate was collected, washed 2x25ml dichloromethane and dried under vacuum, yielding the title product 1.8g (84.7%). Anal. calc. for C_9H_3N: C (86.39), H (2.42), N (11.19). Found: C (85.98), H (2.51), N (11.51).

(2.20) Synthesis of 1,4-diphenyl-but-1,3-diyne

In a 250ml, three necked flask equipped with a thermometer and an inlet for oxygen was placed phenylacetylene (30.6g, 0.3moles) and copper(I) chloride (1g, 0.01moles) in 150ml pyridine. Oxygen (5 bubbles per second) was bubbled through the green stirred solution. After forty-five minutes the temperature had raised to 45°C. After a further two hours the temperature had returned to room temperature. The oxygen was stopped and the mixture was poured onto 250ml water. The resulting

blue solution was extracted with 2x100ml water, dried and concentrated. The collected brown solid was recrystallised from 40-60 petrol, yielding the title product as brown needles, weight 29.1g (96%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 7.3 (m). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 132.432, 129.166, 128.410, 121.701, 81.643, 74.132.

(2.21) Synthesis of 2,5-diphenyl thiophene

In a 1L, round bottomed flask equipped with a stirrer and a reflux condenser was placed 1,4-diphenyl-but-1,3-diyne (20.2g, 0.1moles), an excess of sodium sulphide nonahydrate (60g, 0.3moles) and 500ml methanol. The mixture was refluxed for twenty-six hours. The resulting solution was evaporated to dryness to yield an orange solid, which was washed with 200ml water and left to dry under vacuum, over phosphorus pentoxide. Recrystallisation from ethanol yielded the title compound as orange flakes with a metallic lustre, weight 21.5g (91.3%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 7.71-7.63 (m, 3H), 7.46-7.26 (m, 9H). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 143.594, 134.291, 128.907, 127.494, 125.514, 123.982. MS m/z (relative intensity) 236 (M+ 100), 202 (8), 121 (12).

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2.6 List of Chemicals and Products

2.1 2,6-Pyridinediyldihydrazidine.

2.2 Isophthaloyl dichloride.

2.3 Poly-*N*-acylhydrazine.

2.4 Poly-1,3,4-oxadiazole.

2.5 Poly-1,2,4-triazole.

2.6 2,6-Dicyanopyridine.

2.7 Pyridine-2,6-dicarboxamide.

2.8 2,6-Dibromopyridine.

2.9 2-Cyanopyridine.

2.10 2-Cyanopyridine *N*-oxide.

2.11 1-Methoxy-2-cyanopyridinium methylsulphate.

2.12 2-Cyanopyridine.

2.13 2-Pyridyl hydrazidine.

2.14 Benzoyl chloride.

2.15 *N*-benzoyl-(2-pyridyl) hydrazidine.

2.16 2,6-Diethynylpyridine.

2.17 Poly((2,6'-pyridyl)but-1,3-diyne).

2.18 Poly(2-(2'-thienyl)pyridine).

2.19 Phenylacetylene.

2.20 1,4-Diphenyl-but-1,3-diyne.

2.21 2,5-Diphenylthiophene.

Chapter Three

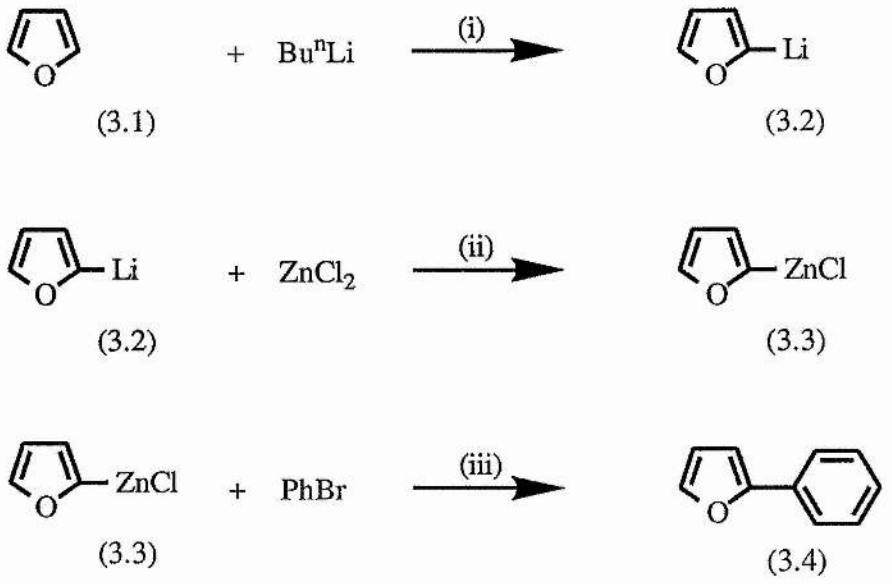
Direct Coupling of Heterocycles

3.1 Introduction

During the work carried out in the preceding Chapter, we realised the shortcomings of the precursor routes, essentially the precursor routes produces polymers which are insoluble, in common solvents, and hence require specialist techniques to convert them to the polymers that were required. It was at this time that we realised that the new methods of directly coupling heterocyclic monomers in the specific 2,2'-manner probably formed the basis of a better strategy to our target polymers. Simply these new methods enabled greater control of the synthetic procedure and hence control of the conformation of the products. The prepared dimers and trimers can be used as the monomers for chemical and electrochemical synthesis of heterocyclic polymers. The dimer and trimer monomers and the subsequent polymers were then tested for their metal binding ability.

3.2 Pyridine-Furan Heterocycles

In 1987, A. Pelter *et. al.*[3.1] at University College Swansea reported a cross-coupling reaction for the preparation of 2-arylfurans. Although the transition metal cross-coupling of organic halides with organometallics[3.2] is well known, the reaction using heterocyclic units is less well known. In the report of the Swansea group, a procedure was given which involved the formation of 2-lithiofuran (3.2) followed by the reaction with zinc chloride to give 2-furyl zinc chloride (3.3). This organometallic



(i) THF / N_2 atmos. / 0°C.

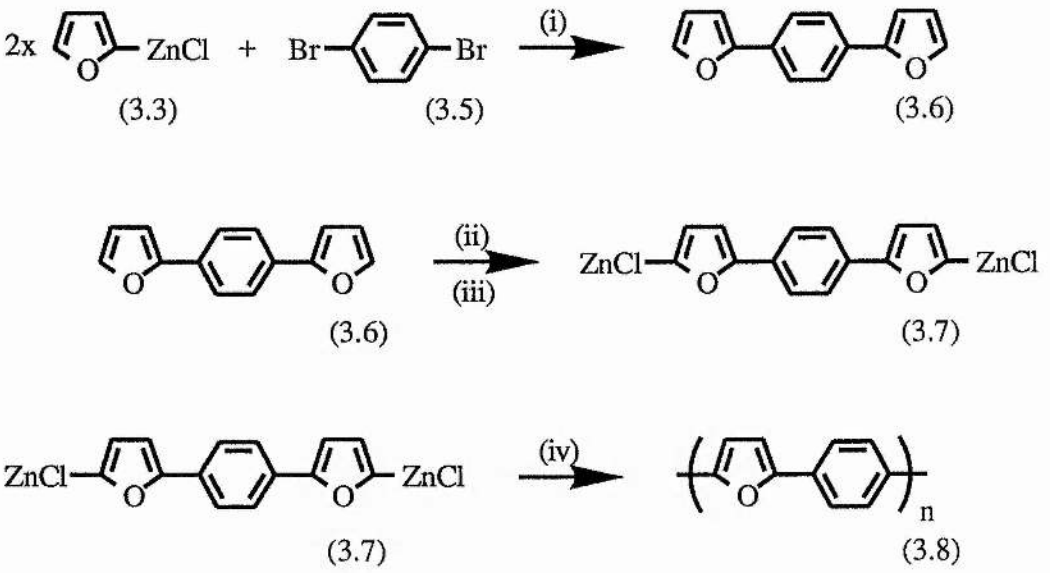
(ii) THF / N_2 atmos.

(iii) THF / N_2 atmos. / 50°C / $Pd(PPh_3)_4$.

Scheme III.I

compound then reacted with an aryl bromide or an aryl dibromide in the presence of a tetrakis(triphenylphosphine) palladium catalyst - Scheme III.I.

In later reports[3.3, 3.4, 3.8] the extension of this reaction to the preparation of polymers based on the same reaction mechanism was discussed. In this case the 2-furyl zinc chloride (3.3) was prepared and reacted with two equivalents of 1,4-dibromobenzene (3.5), to produce 1,4-di-(2-furyl) benzene (3.6). The free furan α-hydrogens were then abstracted to give the bis-metallated compound (3.7). This then reacted with 1,4-dibromobenzene (3.5) to form the polymer (3.8) in a reported yield of 94% - Scheme III.II.



(i) THF / N_2 atmos. / 50°C / $Pd(PPh_3)_4$.

(ii) 2eq. Bu^nLi / THF / 0°C / N_2 atmos.

(iii) 2eq. $ZnCl_2$ / THF / N_2 atmos.

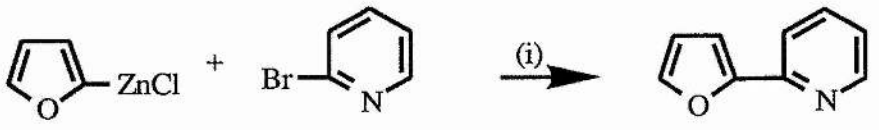
(iv) 1,4-dibromobenzene / THF / N_2 atmos / 50°c / $Pd(PPh_3)_4$.

Scheme III.II

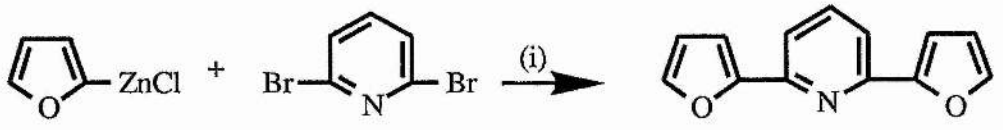
We therefore decided to explore the formation of 2-furyl zinc chloride (3.3) and investigate the coupling to 2-bromopyridine (3.9) and 2,6-dibromopyridine (3.11), in an attempt to prepare dimers and trimers which contain the required 2,2'-heteroatom configuration, thus enabling the investigation of the ability of metals to bind to these ligands.

3.2.1 Synthesis

The Pelter route was thus used to prepare coupled heterocycles containing both furan and pyridine. Molecules prepared were 2-(2-furyl) pyridine (3.10)



(3.3) (3.9) (3.10)



(3.3) (3.11) (3.12)

(i) THF / N_2 atmos. / 50°C / $Pd(PPh_3)_4$.

Scheme III.III

and 2,6-di-(2-furyl) pyridine (3.12) according to the reactions as shown in Scheme III.III.

Both reactions proceeded as described in the literature. 2-(2-Furyl) pyridine (3.10) was prepared in an acceptable yield of 72.4%, as a colourless liquid which darkened somewhat upon storage in direct light. All further preparations were stored in the dark which delayed the onset of the colour change. Characterisation by ^{13}C NMR confirmed the nine aromatic resonances with no trace of other isomers or starting materials, as shown in Figure 3.1(a).

Similarly 2,6-di-(2-furyl) pyridine (3.12) was prepared using the Pelter route. In this case the resultant brown solid was purified, by chromatography on a silica column using petrol:THF (99:1 v/v) as the elutant, followed by recrystallisation from petrol. These processing steps gave the desired product as yellow needles in an acceptable yield of 60.4%. The ^{13}C NMR is outlined in Figure 3.1(b). The seven

aromatic resonances are clearly shown and by comparing them with the spectra for 2-(2-furyl) pyridine (3.10), it is easy to assign the aromatic frequencies for these two compounds.

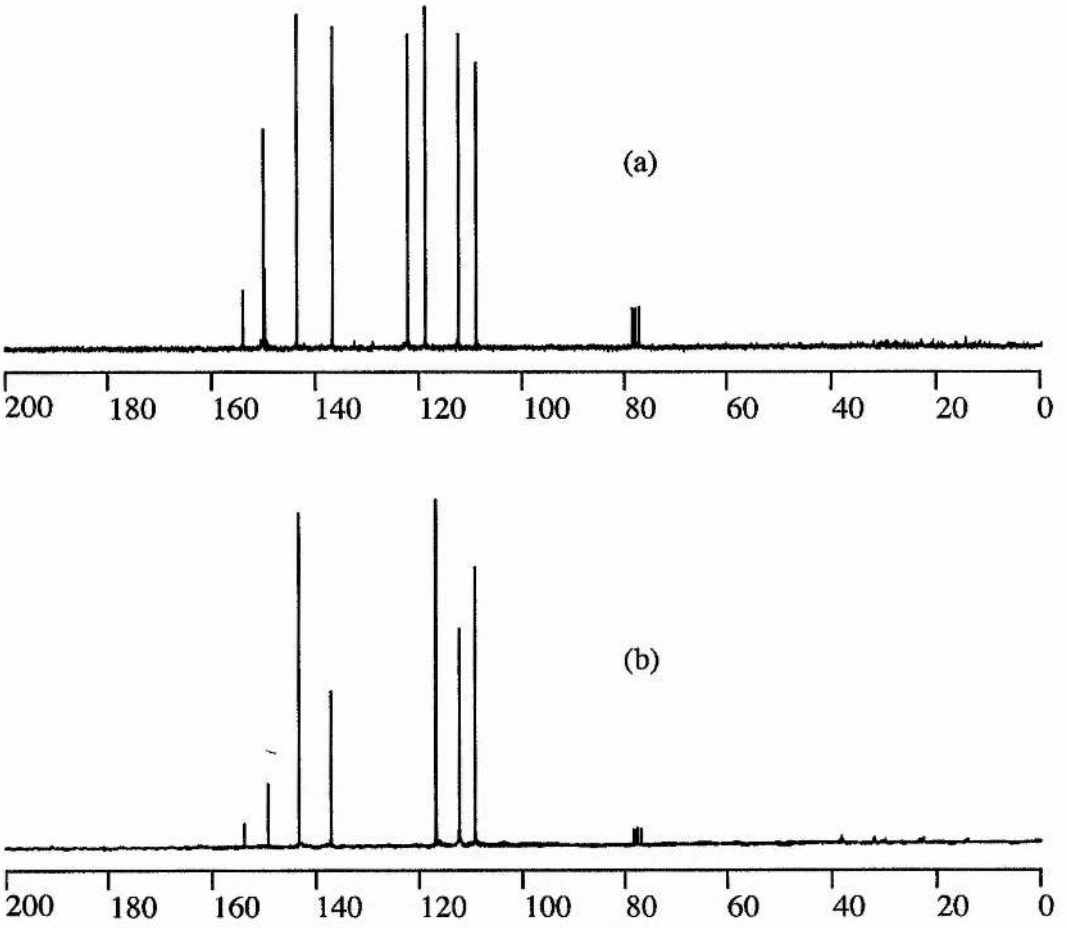
3.2.2 Electrochemistry

In this section we explore the electrochemistry of the pyridine-furan heterocycle, 2,6-di-(2-furyl) pyridine (3.12). The principles of electrochemistry and the exact experimental techniques are discussed in Chapter Five.

There have been no reported electrochemical studies of the monomer, 2,6-di-(2-furyl) pyridine (3.12). Figure 3.2 details the attempted electropolymerisation of the monomer, in acetonitrile / 0.1M TBAT. Figure 3.2(a) is the background scan and by comparing this to Figure 3.2(b), we can see one irreversible anodic peak at +1.6V. The second scan shows a decrease in the height of this anodic peak. It is also noted that the addition of acid causes a shift in the anodic peak to +1.4V, the second scan after the protonation again shows a decrease in the peak height - Figure 3.2(c).

Analysis of the cyclic voltammetry data indicates the formation of an insulating layer during the second scan. Due to the inherent instability of furan rings it is conceivable that a ring opening of one, of more of the furan rings terminates the electropolymerisation reaction. It is therefore assumed that coupling of the second monomer forms a species that is chemically unstable and that this hexamer undergoes a furan ring opening reaction. This oxidative ring opening terminated the delocalised π-system and blocks the addition of any further monomer.

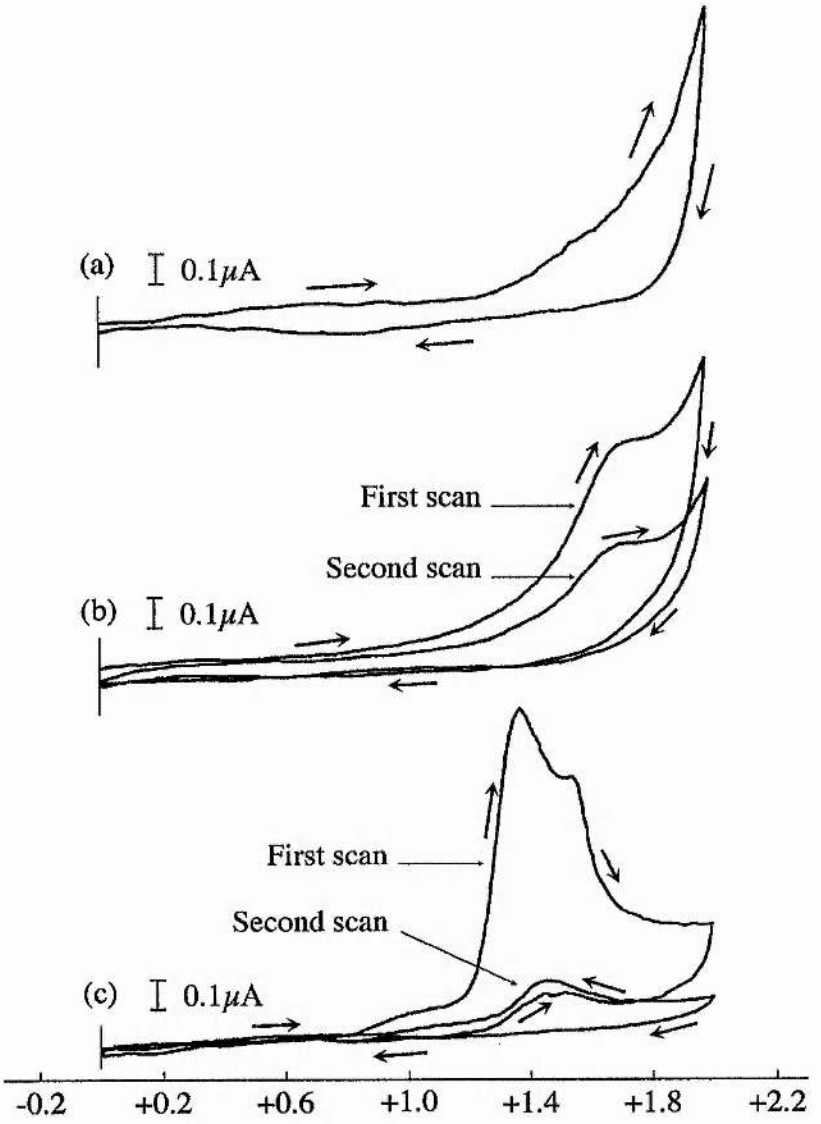
Glenis *et. al.*[3.5] reported a similar ring opening reaction during the formation of polyfuran. Upon spectroscopic analysis of their polyfuran, which was prepared by



^{13}C NMR (50MHz) $\delta(CDCl_3)$ spectra for: (a) 2-(2-furyl) pyridine (3.10); and (b) 2,6-di-(2-furyl) pyridine (3.12).

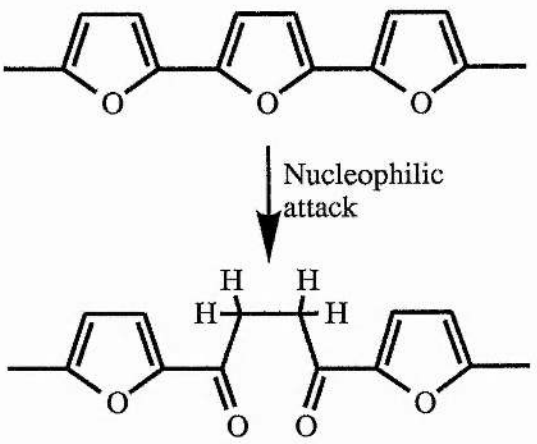
Figure 3.1

the electrochemical oxidation of terfuran, they discovered aliphatic C-H vibrational peaks and characteristic ketone peaks in the infrared spectra. They attribute these abnormal bands to the occurrence of a ring opening of furan. The precise nature of the ring opening is not known for certain. In the paper they report a possible pathway, as outlined in Figure 3.3. The ring opening could be due to the nucleophilic attack on the positively charged α-carbon centres by the dopant and/or water.



CV for the attempted polymerisation of 2,6-di-(2-furyl) pyridine (3.12) in MeCN / 0.1M TBAT: (a) Background scan at $100mVs^{-1}$; (b) First and second scan at $100mVs^{-1}$; and (c) After the addition of trifluoroacetic anhydride (5% v/v).

Figure 3.2

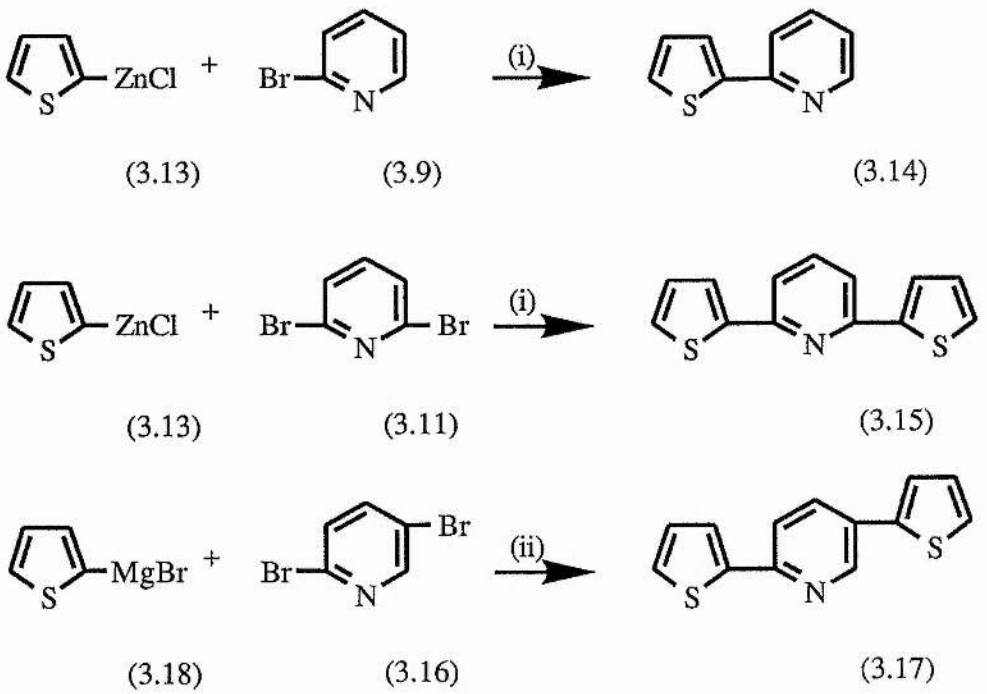


Possible pathway for the ring opening in polyfuran,
as postulated by Glenis *et. al.*[3.5].

Figure 3.3

Unfortunately no spectroscopic investigations of the species being formed during our attempted polymerisation were obtained, but taking the work of Glenis *et. al.*[3.5] into consideration it is conceivable that a similar ring opening reaction occurred after the addition of the second monomer of 2,6-di-(2-furyl) pyridine (3.12).

In this paper they also report that the relative intensity of these aliphatic and carbonyl absorptions was dependent on the counter ion used in the electrochemical doping. Although they do not give a reason for this anomaly they state that the BF_4^- ion is the most damaging to the polyfuran structure. Due to the undesirable characteristics of the furan, compared with thiophene (lower aromaticity, higher ring strain energies and increased reactivity)[3.6], it was considered unfruitful to pursue any further work in this area - such as the electropolymerisation of the monomer 2,6-di-(2-furyl) pyridine (3.12) using less nucleophilic counter ions such as $CF_3SO_3^-$, and to move onto the more promising thiophene containing polymers.



(i) THF / N_2 atmos. / 50°C / $Pd(PPh_3)_4$.

(ii) Et_2O / N_2 atmos. / 0°c / $Ni(dppp)Cl_2$.

Scheme III.IV

3.3 Pyridine-Thiophene Heterocycles

As the synthesis of monomers containing pyridine and furan moieties was so successful, it was decided to continue with the Pelter approach using thiophene instead of furan. The synthesis of 2-lithiothiophene[3.7] has been known for many years and recent reports[3.8] showed that extrapolation to the 2-thienyl zinc chloride (3.13) should proceed as for the 2-furyl zinc chloride (3.3) experiments reported above. In this section we explore the formation of three molecules: 2-(2-thienyl) pyridine (3.14); 2,6-di-(2-thienyl) pyridine (3.15); and 2,5-di-(2-thienyl) pyridine (3.17) as described below and in Scheme III.IV. We prepared the two trimers to

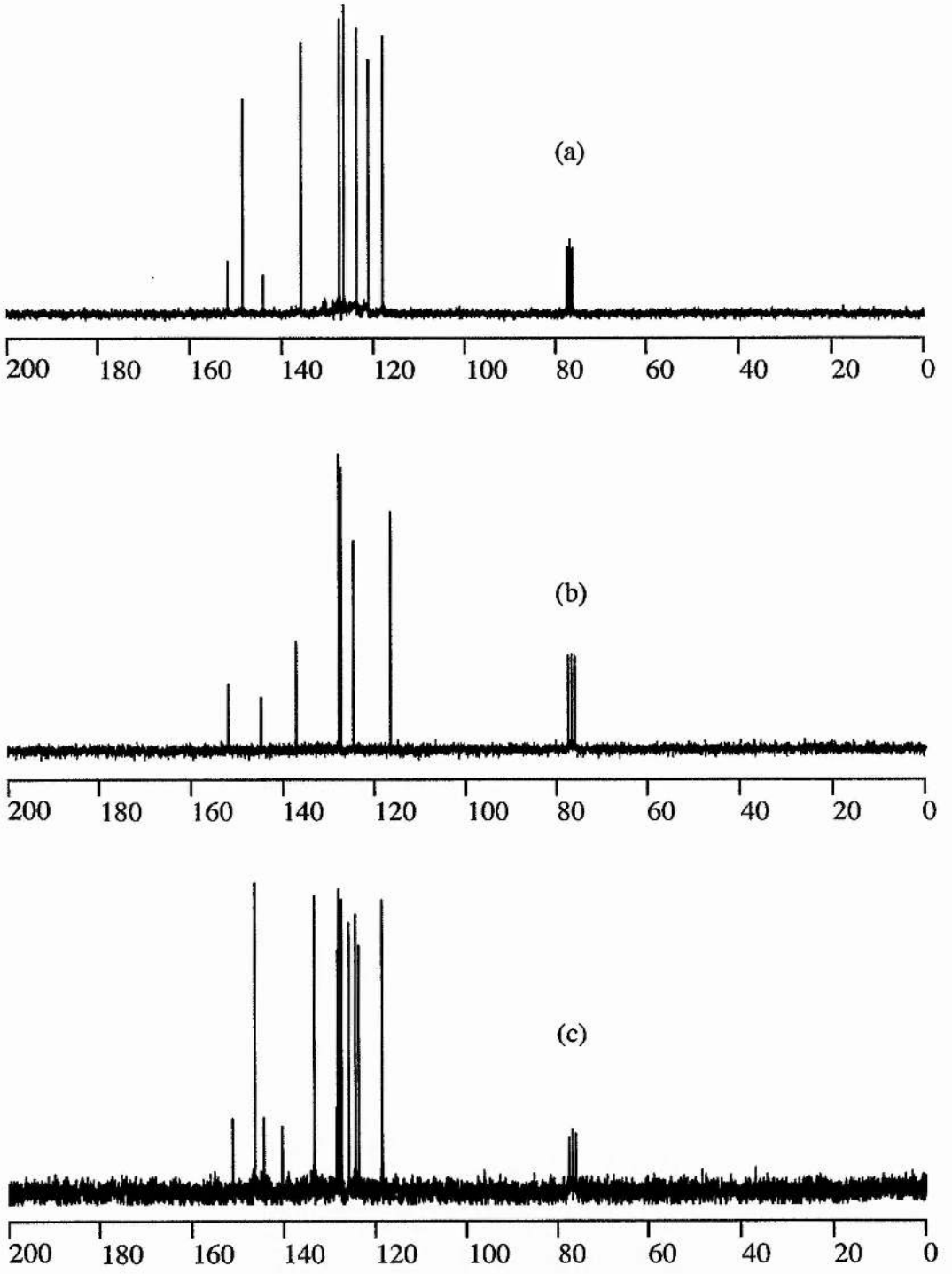
investigate the effects of steric hindrance on the metal binding and on the polymerisation reaction. This is explored in greater detail in Section 3.3.3.

3.3.1 Synthesis

The Pelter route was again successfully used for the preparation of 2-(2-thienyl) pyridine (3.14) and 2,6-di-(2-thienyl) pyridine (3.15). Both compounds were prepared as colourless crystals after careful washing, drying and crystallisation from ethanol. The yields were comparable with those reported[3.9], 56% and 76% respectfully. ^{13}C NMR showed the required nine and seven aromatic resonances and no traces of any starting products or alternative isomers - Figure 3.4(a), 3.4(b). The Pelter route proved unsuccessful for the synthesis of the trimer 2,5-di-(2-thienyl) pyridine (3.17), we therefore had to find another catalytic system which would permit this coupling reaction.

The general cross-coupling of organometallics with organohalides is well known[3.10]. Transition metals, usually nickel or palladium, catalysis these reactions. Figure 3.5 outlines the general cyclic process for the catalytic procedure. Oxidative addition of the organohalides (R-X) with the metal centre of the catalyst (M) forms an organometallic halides (R-M-X). The next step is the transmetallation with the organometallic (R'-M') to provide the diorganometallic complex (R-M'-R'), a reductive elimination reaction leads to carbon-carbon bond formation and regeneration of the catalyst (M). As no analysis of the catalytic procedure were carried out, we can not say why this procedure was unsuccessful. Generally the failure of a process of this type is probably due to failure of one of the oxidation / reduction steps in the cyclic catalytic process.

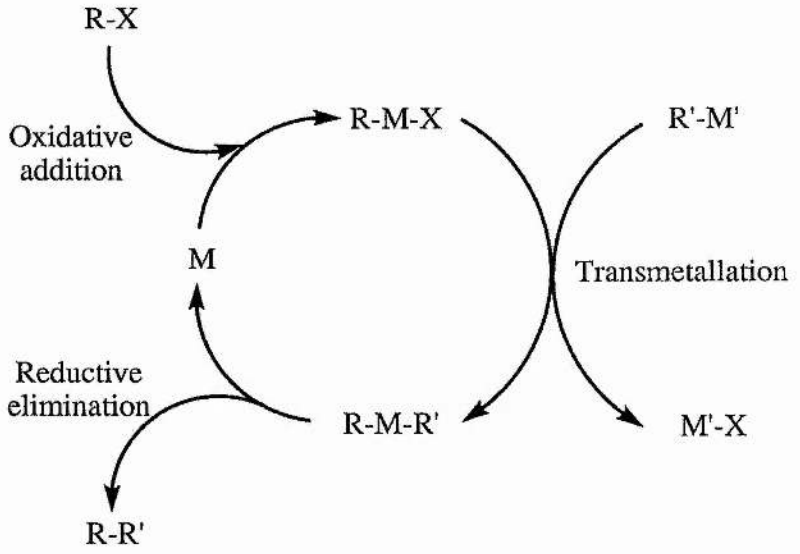
Thus the synthesis of the trimer 2,5-di-(2-thienyl) pyridine (3.17) was



^{13}C NMR (50MHz) $\delta(CDCl_3)$ spectra for: (a) 2-(2-thienyl) pyridine (3.14); (b) 2,6-di-(2-thienyl) pyridine (3.15); and (c) 2,5-di-(2-thienyl) pyridine (3.17).

Figure 3.4

achieved using the Kumada modified Karasch reaction[3.11] as described in Chapter Four for the preparation of polythiophenes. The exact experimental details are described in Section 4.1. Briefly, the procedure involved a nickel catalysed cross-coupling Grignard reaction. The procedure yields the required 2,5-di-(2-thienyl) pyridine (3.17) as yellow needles after recrystallisation from diethylether, in a average yield of 76.3%. Figure 3.4(c) details the ^{13}C NMR of the product and confirms the required thirteen aromatic resonances.



General cyclic process for the cross-coupling of organometallics (R-'M') with organohalides (R-X) using transition metals (M).

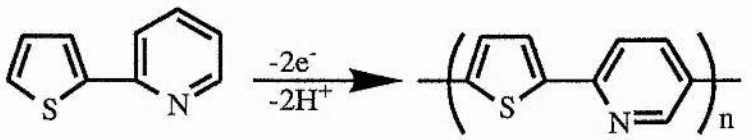
Figure 3.5

3.3.2 Electrochemistry

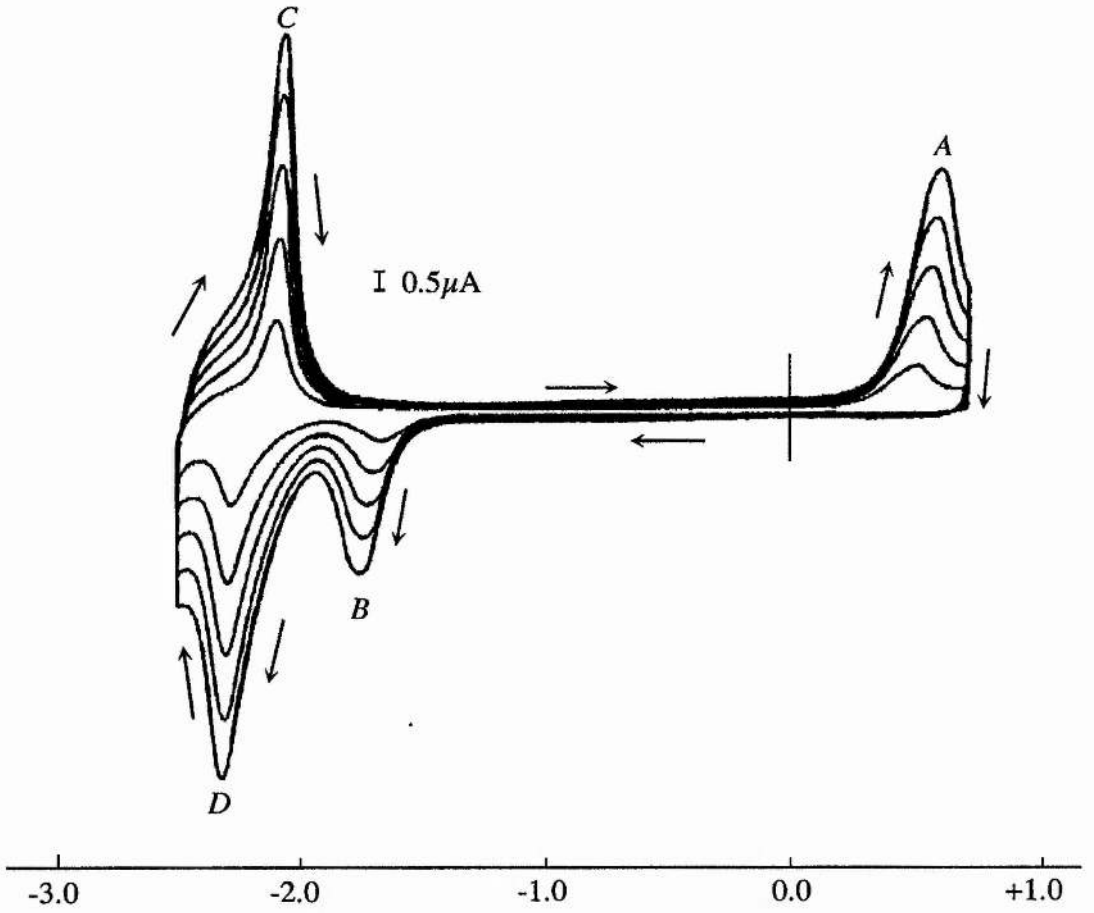
In this section we explore the electrochemistry of the three pyridine-thiophene molecules prepared: (a) 2-(2-thienyl) pyridine (3.14); (b) 2,6-di-(2-thienyl) pyridine (3.15); and (c) 2,5-di-(2-thienyl) pyridine (3.17). Particular importance is placed on

the investigation of the metal binding properties of the two trimers. These investigation are expanded in Section 3.3.3, where we compare the X-ray data for the two trimers. As mentioned previously the principles of electrochemistry and the exact experimental techniques are discussed in Chapter Five.

(a) The electrochemistry of 2-(2-thienyl) pyridine (3.14):- In 1991 T. Yamamoto *et. al.*[3.12] reported the optical and electrochemical properties of π-conjugated copolymers, which included π-excessive thiophene-2,5-diyl and π-deficient pyridine-2,5-diyl units. The polymers were prepared by chemical polymerisation via a $Ni(cod)_2$ catalysed procedure[3.13]. A formic acid solution of the polymer was painted onto Pt plates and by drying these plates *in vacuo*, the polymer films were obtained. Our polymer was prepared by the simple electropolymerisation technique, as described in Chapter Five. It is clear from a comparison between the cyclic voltammograms of our polymer and the chemically synthesised one, as reported by Yamamoto *et. al.*[3.12], that the monomer 2-(2-thienyl) pyridine (3.14) has coupled in the following manner:-



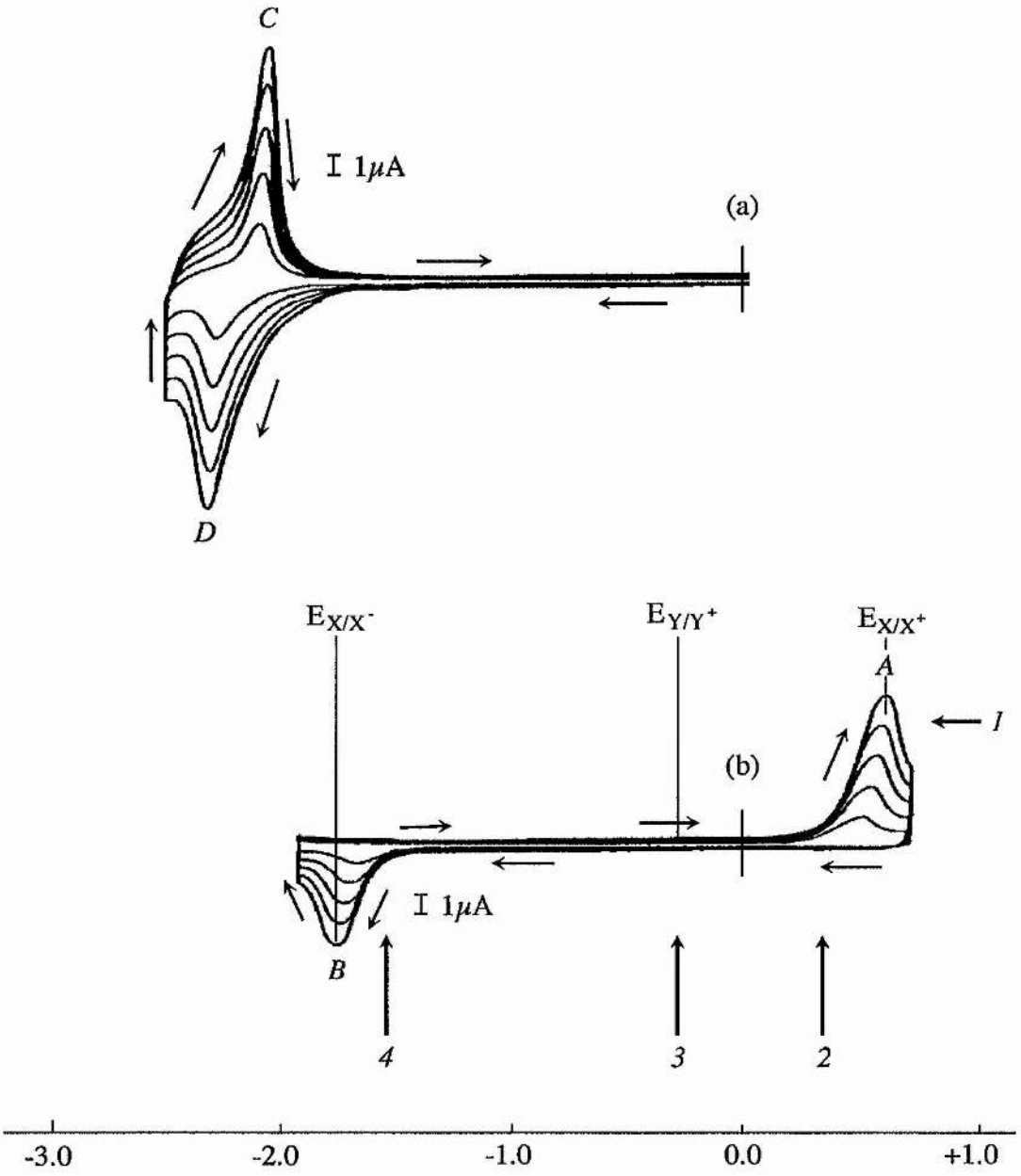
The polymer coated test electrode was carefully washed, to remove any monomer, and then placed in a fresh electrochemical cell. Figure 3.6 shows the CV for polymer obtained from 2-(2-thienyl) pyridine (3.14) in MeCN / 0.1M TBAT sweeping between -2.5V and +0.7V and at scan rates 20-100mVs^{-1}. The CV peak heights increase linearly with increasing scan rate. Our results concur with those of Yamamoto *et. al.*[3.12]. The CV swept in the potential range of -2.5V and +0.7V clearly shows four peaks. There are two anodic peaks at +0.6V (*A*) and -2.1V (*C*), and two cathodic peaks -1.6V (*B*) and -2.3V (*D*).



CV for the electrochemically prepared polymer from the monomer 2-(2-thienyl) pyridine (3.14) in MeCN / 0.1M TBAT. Potential limited between -2.5V and 0.7V, and at scan rates 20-100mVs^{-1}.

Figure 3.6

There are many unique phenomenon associated with this system. Firstly, if the potential scan is limited to the potential region -2.0V to +0.7V then the polymer is inert, i.e. no peaks are observed. Upon expanding the potential range to -2.5V we start to observe the *C-D* couple. To obtain the *A-B* couple the potential must be swept to +0.7V, after taking it negative to -2.5V. Figure 3.7(a) shows the CV in the

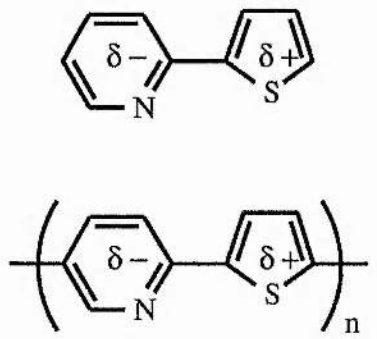


CV for polymer prepared from the monomer 2-(2-thienyl) pyridine (3.14) in MeCN / 0.1M TBAT: (a) potential limits -2.5V to 0.0V, for scan rates 20-100mVs^{-1}; and (b) potential limits -1.9V to +0.7V, for scan rates 20-100mVs^{-1}.

Figure 3.7

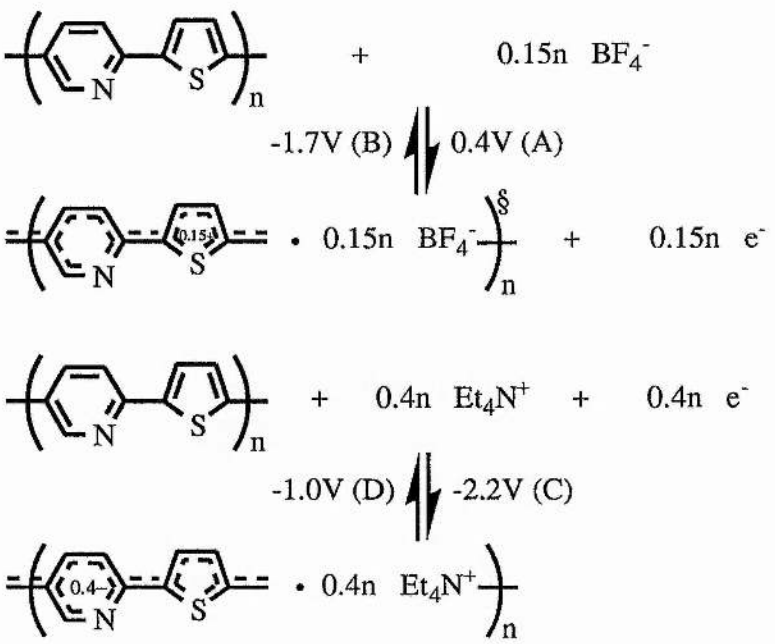
potential region -2.5V and 0.0V. It can be clearly seen that the reverse peak *B* is absent. The reverse couple peak *B* only appears when the anodic peak *A* has first been initiated - Figure 3.6. If the potential is, at least once, taken to -2.5V and then advanced to +0.7V then the couple *A*-*B* becomes observable. The reason for these unique phenomenon is not known for certain, but one can assume that the physical and chemical changes of the polymer, which trigger the electrochemical reaction of the polymer at the thiophene ring, probably take place after n-type doping of the pyridine ring. This doping promotes the injection of cations and solvent into the polymer, which then facilitates the oxidation process.

Before considering further the electrochemistry of the polymer, we shall first consider the monomer 2-(2-thienyl) pyridine (3.14). It is well known that thiophene rings are π-excessive[3.14], whereas pyridine rings are π-deficient[3.15]. Taking this into account it is conceivable that the polymer will exhibit some form of intramolecular charge transfer, Figure 3.8 outlines this intramolecular charge transfer. Such polarisation has been proposed as a basis of the chemical properties of the corresponding monomer, 2-(2-thienyl) pyridine (3.14).



Comparison of the polarisation of the monomer 2-(2-thienyl) pyridine (3.14) and the electrochemically produced polymer.

Figure 3.8



Taken from Yamamoto *et. al.*[3.25]. Equations indicating the oxidation and reduction potentials of the thiophene rings (couple *A-B*) and the pyridine units (couple *C-D*).

§ This species is considered to undergo reduction at -1.6V after certain chemical changes (EC mechanism, see text).

Figure 3.9

Peak *A* at +0.6V, can be attributed to the oxidation of the thiophene moieties within the polymer chain. Polythiophene has reported oxidation potentials in the region +0.67V / +0.69V[3.16]. Peak *B* at -1.6V, initially presents some problems in determining it significance, and we shall discuss this peak later. The positions of peak *C* and peak *D*, correspond closely with the reported doping and undoping potentials of polypyridine (-2.58V and -2.19V, respectively)[3.17]. To confirm that peaks *A-B* and peaks *C-D* are related couples, cyclic voltammograms were obtained by ending the potential sweep at -1.9V. Figure 3.7(b) shows the cyclic voltammogram in the potential region -1.9V to +0.7V. It is noted that only the couple *A-B* is observed.

Assuming that these two peaks are related then why is there such a large potential difference between the two peaks? One must assume that there is some electrochemical mechanism taking place after the oxidation of the thiophene ring. It has been postulated that a shift of a lone pair of electrons from the pyridine ring to the positively charged thiophene ring occurs with the corresponding shift of a counter anion (BF_4^- in our example - see Figure 3.9) to afford a different doping state[3.25]. Thus it is conceivable that the unique switching effect observed for the *A-B* couple may be accounted for by such an electrochemical mechanism.

Similar CV's showing large peak separations have been observed in 'charge-transfer' salts such as $TTFBr_x$ (TTF = tetrathiafulvalene)[3.26]. The peak separation is associated with a major structural change and reflects changes in the lattice energy of the salt. Such a similarity provides further evidence in support of the intra-chain 'charge-transfer' as depicted in Figure 3.8. Thus this large peak separation could be due to a large conformational change in the polymer, rather than a lattice energy change. In addition to this postulated explanation for the CV's we might consider 'charge-trapping'. This phenomenon has been investigated by Murray[3.27]. Simply, for a thick polymer coated electrode we find that there are different environments within the polymer chain. For 'charge-trapping' to occur, the layer closest to the electrode (inner layer X) must have a higher oxidation potential than the polymer furthest from the electrode (outer layer Y).

$$E_{\underset{(INNER)}{X/X^+}} > E_{\underset{(OUTER)}{Y^+/Y}} \qquad \text{Eq: 3.1}$$

With reference to Figure 3.7(b), consider the four reference points marked *1* to *4*. At point *1* the whole film is oxidised thus,

$$X^+ + Y \longrightarrow X + Y^+ \qquad \text{Eq: 3.2}$$

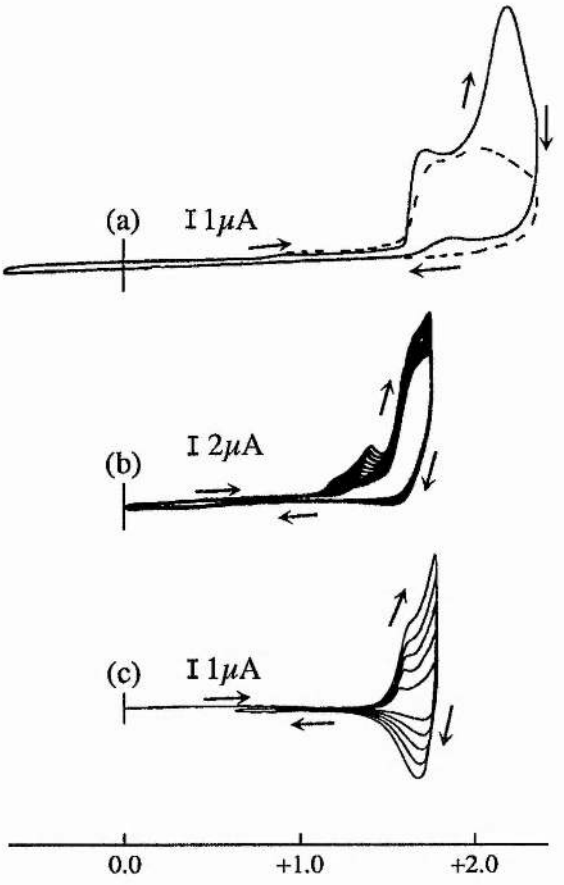
At point *2*, X is reduced and forms an insulating layer. As we sweep through *3*, we reach a point at which Y^+ is thermodynamically capable of being reduced but the insulating layer of X prevents it. Thus the charge, Y^+ is trapped. As we reach point *4*, the point at which X becomes sufficiently conducting (n-doping?), this allows the untrapping of the charge and both X and Y are thus reduced.

$$X^- + Y^+ \longrightarrow X + Y \qquad \text{Eq: 3.3}$$

(b) The electrochemistry of 2,6-di-(2-thienyl) pyridine (3.15):- The electrochemistry has been briefly described by Tanaka *et. al.*[3.18]. Figure 3.10(a) shows the CV for 2,6-di-(2-thienyl) pyridine (3.15) in MeCN / 0.1M TBAT at a Pt electrode. There are two irreversible anodic peaks at +1.6V and +2.1V. When the anodic limit of the scan is set to just beyond the first peak there is steady build-up of current due to electropolymerisation - Figure 3.10(b). However, it should be noted that scanning over the second wave at +2.1V leads to rapid electrode passivation (i.e. the current decays to zero). Visual examination of the electrode confirms the presence of conducting polymer which is yellow at low coverages and copper-coloured for thick films. Transferring the polymer coated electrode to monomer-free electrolyte allows one to observe both anodic and cathodic polymer waves at Ep^a +1.5V and Ep^c +1.6V whose heights increase approximately linearly with scan rates - Figure 3.10(c).

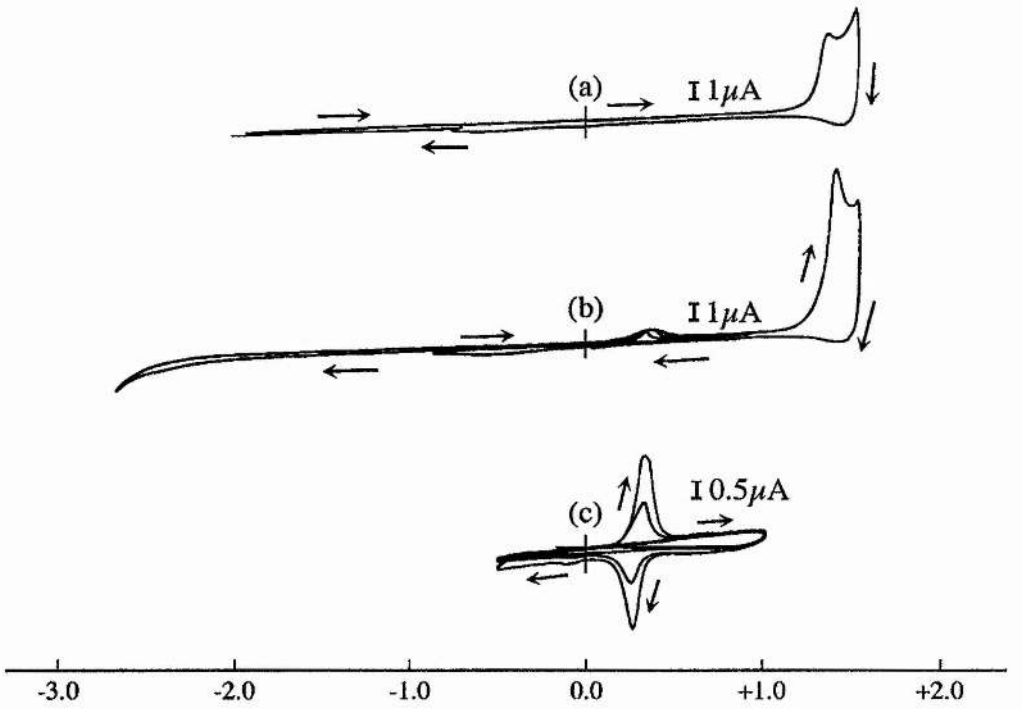
The relatively high potentials necessary to oxidise both the monomer and polymer are consistent with the MO calculations showing a higher energy HOMO for 2,6-di-(2-thienyl) pyridine (3.15). This is explored further in Section 3.3.3. Also we see no n-doping peaks for this polymer, the reason seems to be that a break-in period to allow introduction of the relatively bulky R_4N^+ cation into the compact polymer. Pickup *et. al.*[3.19] showed that at least 20 cycles were necessary before the n-doping

peak appeared at -1.75V; we see a similar broad peak centred at -2.0V which is very weak after just one scan (Figure 3.11).



CV for 5mM 2,6-di-(2-thienyl) pyridine (3.15) in MeCN / 0.1M TBAT: (a) First scan (——) and second scan (- - -) at 200mV/s; (b) electropolymerisation with anodic limit of +1.7V; and (c) polymer CV in fresh MeCN / 0.1M TBAT, for scan rates 20-100mV/s.

Figure 3.10

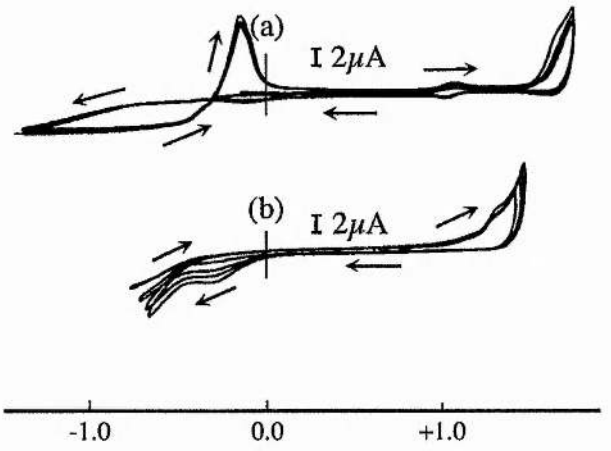


CV for poly-(2,6-bis-(2-thienyl) pyridine) (3.19) in MeCN / 0.1M TBAT at 200mV/s, in the presence of 0.1mM $AgCF_3SO_3$: (a) -2.0V cathodic limit; (b) -2.7V cathodic limit; and (c) $Ag^{0/+}$ wave after brief removal from solution.

Figure 3.11

In order to incorporate metal ions into this conducting polymer we required the polymer to be conducting towards dissolved metal ion redox couples. However, the as-formed polymer is completely insulating, as tested with an external redox couple, over a wide range of potentials in acetonitrile containing 0.1mM Ag CF_3SO_3 - Figure 3.11(a). It is only after widening the cathodic scan to in excess of -2.7V that one sees the Ag/Ag^+ redox couple - Figure 3.11(b). This phenomenon is probably related to

Pickup's break-in observation[3.19], this time with Ag^+ replacing R_4N^+ as the break-in cation. Interestingly, if the electrode is taken out of the solution (and out of potential control) for a few seconds and then replaced the Ag/Ag^+ couple is enhanced - Figure 3.11(c). The $Ag^{0/+}$ wave then dies away once more. The reason for this is not clear as O_2 bubbling or light exposure while the electrode was in solution did not have the same effect as electrode removal. The best explanation appears to be that the polymer is momentarily oxidised by oxygen and moisture to a more conducting film.



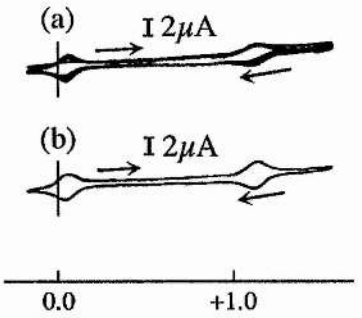
CV for poly-(2,6-bis-(2-thienyl) pyridine) (3.19) in MeCN / 0.1M TBAT at 200mV/s: (a) 1mM $Cu(ClO_4)_2$; and (b) 1mM $PdCl_2$.

Figure 3.12

Similar behaviour was observed for the $Cu^{0/+}$ redox couple (stripping wave at -0.14V and $Cu^{2+/+}$ couple at +1.0V, Figure 3.12(a)). Pd^{2+} reduction waves also grew in steadily at -0.3V after an initial cathodic excursion to -1.2V - Figure 3.12(b). In all of these cases, there was little change in the polymer wave at +1.5V although the wave did sometimes appear broader and shifted towards a more negative potential. We

therefore assume that metal deposition is occurring on the electrode surface which is only reachable after the structure of the polymer is opened up by cation insertion at cathodic potentials, similar results were noted by Pickup *et. al.*[3.19].

Finally, we wished to examine whether soluble metal complexes could be incorporated within the polymer either by ion-exchange (e.g. $[Fe(CN)_6]^{3-}$) or by pyridine binding (e.g. $[Ru(edtaH)]Cl]^-$). However, there was no evidence from the CV of the polymer in the presence of these redox couples that any incorporation was taking place. There could be several reasons for this including the steric hindrance around the pyridine donor nitrogen atom or, more likely, giving the discussion above, the insulating hydrophobic nature of the polymer. However, using $[Ru_3O(OAc)_6py_2(MeOH)]^+$, a redox couple which binds to pyridine under non-aqueous conditions, we were able to observe apparently surface confinement of the redox waves at +0.04V and +1.04V - Figure 3.13.



CV for poly-(2,6-bis-(2-thienyl) pyridine) (3.19) in MeCN / 0.1M TBAT at 200mV/s: (a) 1mM $Ru_3O(OAc)_6py_2MeOH$; and (b) in fresh MeCN / 0.1M TBAT.

Figure 3.13

These waves developed very small ΔEp values and lost their diffusional "tails". However the coverage was extremely low, corresponding to about a monolayer. The peaks persisted for 2-3 cycles after transferring to pure MeCN electrolyte. It is not yet clear whether this complex is adsorbing at the electrode-polymer interface or at the polymer solution interface.

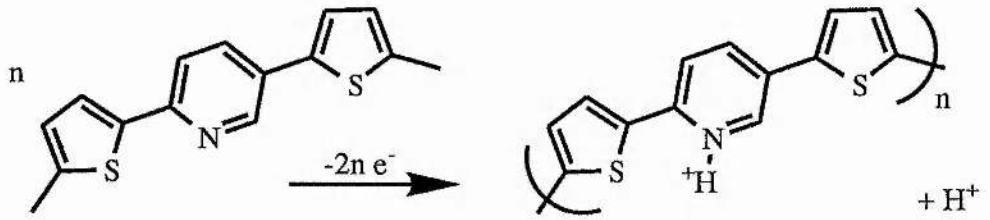
In summary, the conducting polymer poly(2,6-bis-(2-thienyl) pyridine) (3.19) was investigated as a possible host for binding metal complexes. However, the conducting regime of the polymer is at extremely positive potential (>+1.4V) and the polymer is hydrophobic. Cathodic sweeps of the polymer led to greater electroactivity due to 'break-in' of solvent and R_4N^+ cations[3.19], and including potentials where Cu, Pd and Ag are electrodeposited. There was no evidence for extensive binding to the pyridine sites within the polymer, but a Ru trimeric complex was adsorbed as a monolayer.

(c) The electrochemistry of 2,5-di-(2-thienyl) pyridine (3.17):- The electrochemical polymerisation has been briefly described by Tanaka[3.18] and Pickup *et. al.*[3.19]. Figure 3.14(a) details the CV for 2,5-di-(2-thienyl) pyridine (3.17) in acetonitrile / 0.1M TBAT at a Pt electrode. We see at least three oxidation waves at +1.30V, +1.65V and +1.85V. The first of these is likely to be the one-electron oxidation of the monomer to produce thiophene radical cations. The more positive peaks represent the further oxidation of oligomeric species. Such overoxidation has been previously shown to be detrimental to polymer formation - as reported above for the electropolymerisation of the monomer 2,6-di-(2-thienyl) pyridine (3.15). Therefore similarly we applied an anodic limit of +1.30V and upon cycling we started to see the current increase indicative of electropolymerisation -Figure 3.14(b).

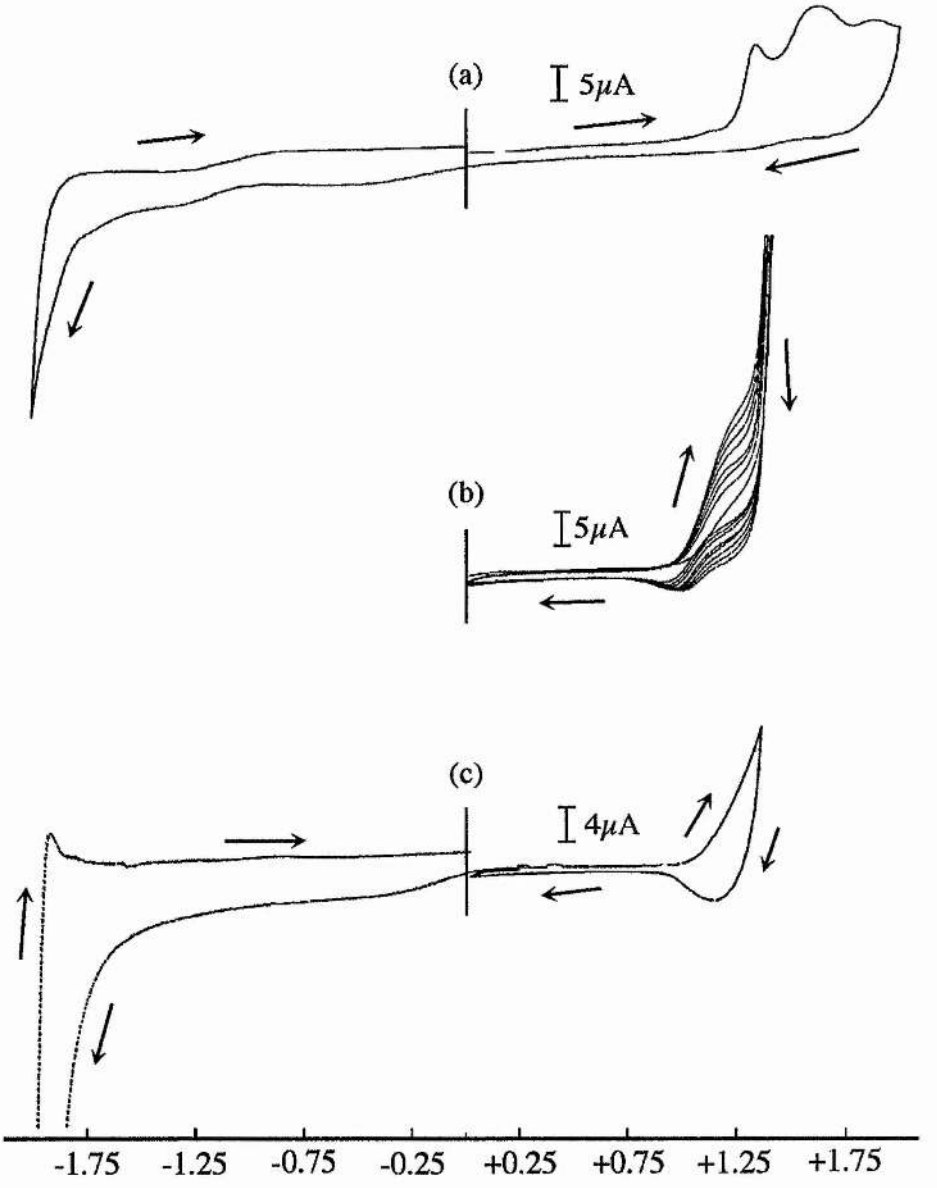
The polymer CV (Figure 3.14(c)) fails to show a peak for the oxidation but a broad cathodic peak (E_p^c +1.0V) is observed. Similarly Pickup *et. al.*[3.19] observed

this effect and explained the lower potential compared to the 2,6- isomer in terms of the HOMO energies (this is further discussed in Section 3.3.3), it is also noted that p-doped coordination energies are higher for the 2,5- isomer than the 2,6- isomer. They also report an n-doping wave at -1.80V, which we were unable to reproduce, but we did observe large cathodic currents at this potential with some small anodic return at -1.70V. Our polymer was prepared by potential cycling, rather than galvanostatic, as reported by Pickup *et. al.*[3.19], therefore this could account for the irreproducibility. When we used the galvanostatic method (0.8mAcm^{-2} for 400s, potential ≤1.20V) we obtained a substantially thicker polymer film - Figure 3.15(a). These films had an anodic wave at lower potential (+1.00V) and better defined than that grown by potential cycling. The CV is quite similar to that observed by Pickup *et. al.*[3.19].

Even this new, galvanostatically produced polymer, initially gave large cathodic currents which eventually subsided - Figure 3.15(a). Pickup *et. al.*[3.19] also noticed the different 'break-in scans' effect in which the cathodic current gradually increases with each cycle (it became stable after 13 scans). We propose that these large cathodic currents are due to reduction of protons on the pyridine groups of the polymer. These protons were of course produced by the polymerisation reaction, as outlined below:-

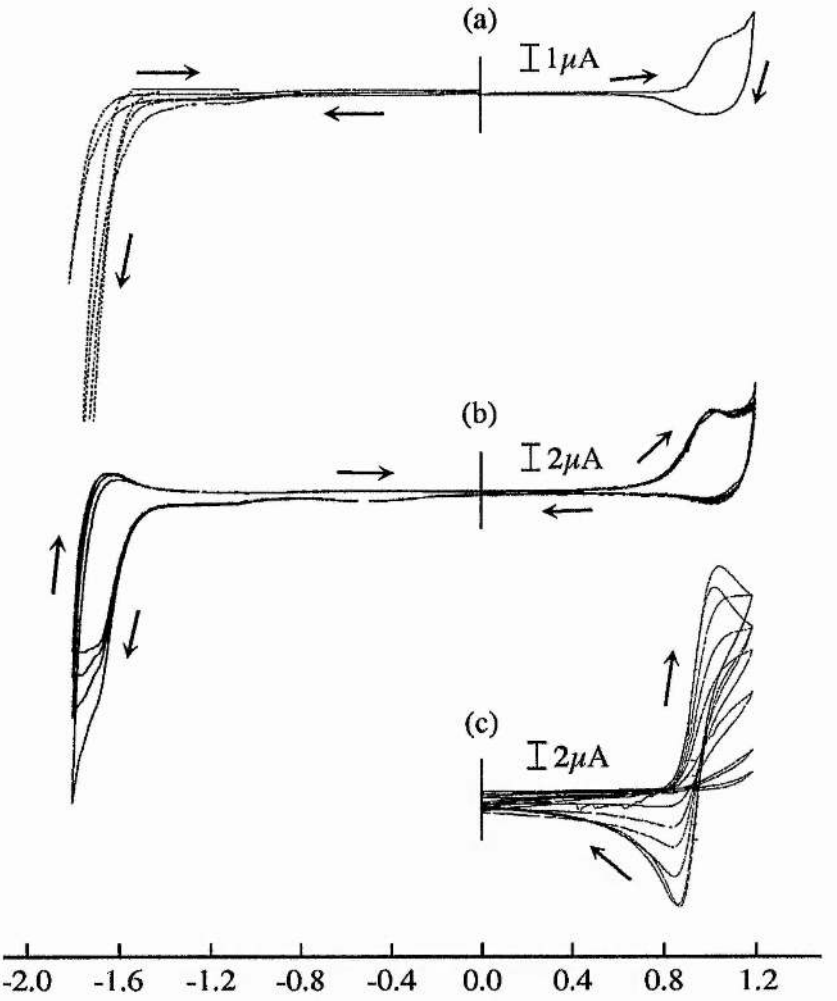


One piece of evidence to support this assumption is that when polymerisation is carried out in the presence of $K_2[Ru^{II}(edta)Cl]$ the cathodic currents were substantially less and the anodic peak was better defined - Figure 3.15(b). The cathodic peak which



CV for **potential cycling** of 10mM 2,5-di-(2-thienyl) pyridine (3.17) in MeCN / 0.1M TBAT: (a) First scan at 100mV/s; (b) electropolymerisation with anodic limit of +1.3V, scans 1 to 8 at 100mV/s; and (c) CV of polymer prepared by potential cycling in fresh MeCN / 0.1M TBAT.

Figure 3.14



(a) CV for the **galvanostatic** electropolymerisation of 10mM 2,5-di-(2-thienyl) pyridine (3.17) in MeCN / 0.1M TBAT. The negative traces are showing that the current becomes less on each successive scan; (b) CV for the galvanostatic electropolymerisation as above, but in the presence of 5mM $K_2[Ru(edta)Cl]$. The negative trace show the current decreasing; and (c) CV of galvanostatically produced poly-(2,5-dithienylpyridine) after addition of 10mM $Cu(MeCN)_4BF_4$. The CV gradually increases in height.

Figure 3.15

has developed is probably polymer but could contain a contribution from the $Ru^{III/II}$ redox process. Lindall *et. al.*[3.20] have shown that this couple shifts substantially negative on binding to pyridine groups in acetonitrile.

The realisation that solvation of the polymer and protonation of the pyridine groups may be interfering with our studies of any possible coordination properties helps to explain the somewhat variable results that we have obtained. One such example is shown by the CV in Figure 3.15(b) which appeared to show strong coordination of $Cu(MeCN)_4^+$ to the polymer, giving a $Cu^{2+/+}$ wave near +0.95V. Unfortunately, this behaviour was not readily reproducible. However, the polymer in Figure 3.15(c) had been thoroughly cycled and almost deactivated. With hindsight this polymer may thus have been protonated. Further studies with fully deprotonated polymer (prepared by soaking in pyridine, for example) will be necessary in order to fully elucidate the properties of the polymer.

3.3.3 X-Ray Analysis - Comparison of 2,5-Di-(2-Thienyl) Pyridine and 2,6-Di-(2-Thienyl) Pyridine

Appendix One (page 189) details the X-ray structure report for the trimer 2,5-di-(2-thienyl) pyridine (3.17) - some of the Figures and Tables refered to here, can be found in the Appendix. Unfortunately no reported X-ray structures for the isomer, 2,6-di-(2-thienyl) pyridine (3.15), could be found in literature. Therefore we were unable to make any comparisons between the two trimers. Thus in this section we shall only give a brief summary of the X-ray data.

Jenkins *et. al.*[3.19] performed *ab. initio.* calculations on the 2,5-di-(2-thienyl) pyridine (3.17) and the 2,6-di-(2-thienyl) pyridine (3.15) isomers using Gaussian 92 / DFT. The programs use the local spin density approximation which is

known to underestimate HOMO-LUMO gaps, but this was corrected using correlation corrections. The HOMO-LUMO energies are shown in Figure 3.16 and are compared to the electrochemical and optical data. Similar correlations were observed in a previous paper from St. Andrews on quinone derivatives[3.21].

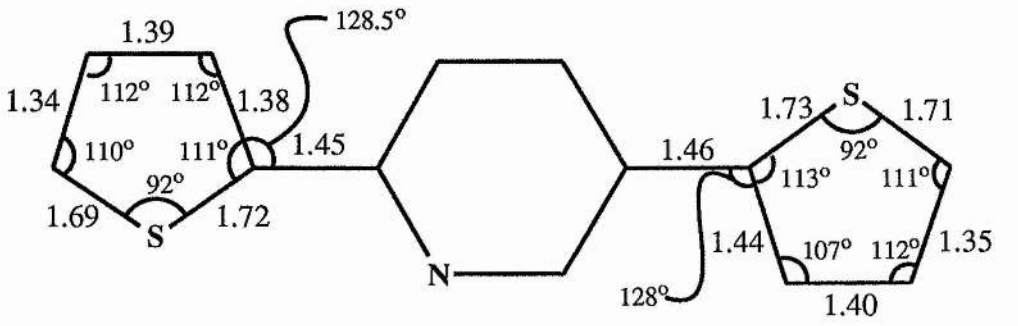
However it should be noted that the calculated HOMO energies are thought to correlate well with redox potentials for oxidation but LUMO energies correlate less well with the reductions. This is because LUMO energies do not provide very good estimates for the electron affinities. The theoretical HOMO-LUMO gaps are 0.3-0.5eV higher than the electrochemical gaps which are in turn 0.1-0.3eV higher than the optical gaps. The large bandgap of the 2,6-di-(2-thienyl) pyridine (3.15) isomer is mainly due to the higher energy of the LUMO (i.e. harder to reduce). Natural bond orbital (NBO) analysis shows that although this isomer exhibits a larger total π-delocalisation, it has weaker π-delocalisation between the individual rings than in the 2,5-di-(2-thienyl) pyridine (3.17) isomer. We were therefore interested to see whether the crystal structure of the 2,5-di-(2-thienyl) pyridine (3.17) isomer provided

Monomer	***Ab. initio.* calculations**			**Electrochemistry**			**Optical**
	E_{HOMO}	E_{LUMO}	gap	E_p^a, ox	E_p^a, red	ΔE	
2,6-	+5.95	-1.84	4.18[a]	+1.46	-2.26	3.72	3.43
2,5-	+5.82	-2.08	3.70[a]	+1.35	-2.08	3.43	3.32

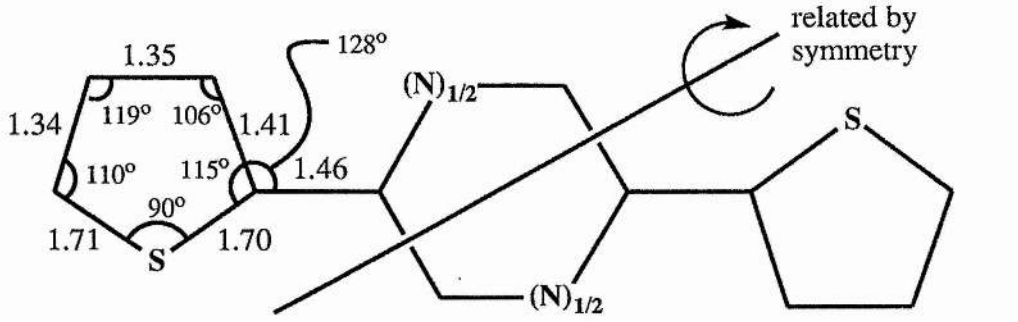
Comparison of the theoretical, electrochemical and optical band gaps(eV) for the two trimers: 2,6-di-(2-thienyl) pyridine (3.15); and 2,5-di-(2-thienyl) pyridine (3.17). These values are obtained from Jenkins *et. al.*[3.19].

[a] Note there seems to be a small error in these values in the paper[3.19].

Figure 3.16



Molecule A



Molecule B

Bond lengths and bond angles for the two molecular types of the monomer 2,5-di-(2-thienyl) pyridine (3.17).

Figure 3.17

structural evidence for this in the bond-lengths of the ring linking C-C bonds or whether this isomer exhibits greater planarity. Unfortunately, we have not been successful in growing suitable single crystals of the 2,6-di-(2-thienyl) pyridine (3.15) isomer. Thus, in the following discussion comparisons are made to oligothiophenes.

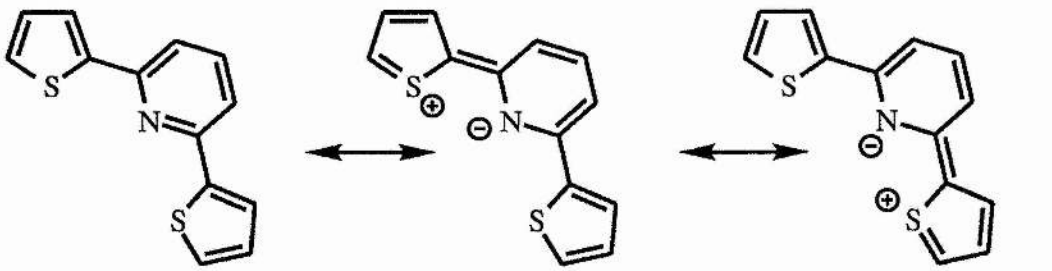
Accordingly, we find that the 2,5-di-(2-thienyl) pyridine (3.17) isomer crystallises in the $P2_{1/C}$ space group. There are two molecules in the unit cell, one of which (molecule B) has a pseudo centre of symmetry due to disorder in the nitrogen

position (Figure 3.20). Firstly if we examine the thienyl bond lengths and angles (Tables 3.3 and 3.5 respectively) we observe the geometry as depicted in Figure 3.17.

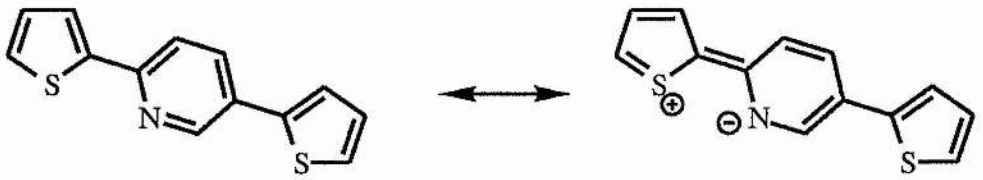
It is noted that for sexithiophene[3.22] and octithiophene[3.23] the outer thiophenes have C=S and C-S bonds which are slightly shorter than the other bonds. Our structure has anomolously long inner C=C thienyl bond lengths due to the large thermal ellipsoids of the atoms C12 and C15. The reason for this becomes apparent when the molecules are seen to be non-planer with puckering of the thienyl rings with S pointing towards a CH due to steric interactions. In fact the torsion angles between rings are 7° (molecule A) or 5° (molecule B, which is disordered between two states) - Figure 3.21. This compares with 1° or less for the left hand side of molecule A and 0.0-1.2° for sexithiophene. Despite this the relative planarity of the molecule allows then to stack together in the normal herringbone pattern (Figure 3.22).

Similarly Ghosh and Simonsen[3.24] reported for the dimer, 2-(2-thienyl) pyridine (3.14), that the bond length C4'-C5 (bond between the two rings) is a partial double bond. This resulted from the conjugation of the two rings and held the molecule almost planer. They also reported a slight twist (<1°) across this partial double bond which they attributed to the intramolecular short contact between S and N.

One would expect the puckering in the 2,6-di-(2-thienyl) pyridine (3.15) isomer to be less since both thienyl rings may point towards the N rather than C-H. Another reason is of course the possibility of charge transfer interactions between the rings[3.9, 3.12, 3.25]. Certainly the C-C bond connecting the conjugated thienyl ring in molecule A is significantly shorter. Thus the greater stabilisation of the 2,6-di-(2-thienyl) pyridine (3.15) isomer through interactions with both thiophene groups would be expected to increase its HOMO-LUMO gap as observed - Figure 3.18.



(3.15)



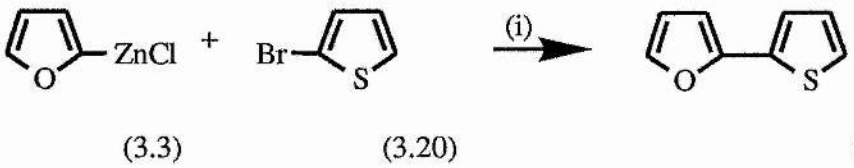
(3.17)

Charge transfer interaction between the rings for the two trimers: 2,6-di-(2-thienyl) pyridine (3.15) - top; and 2,5-di-(2-thienyl) pyridine (3.17) - bottom.

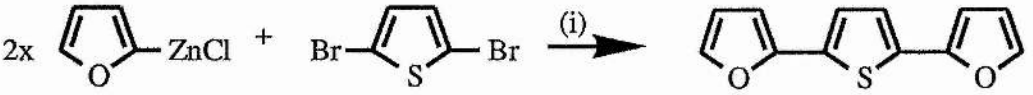
Figure 3.18

3.4 Thiophene-Furan Heterocycles

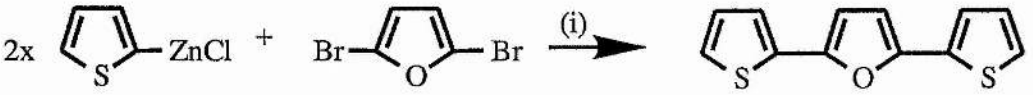
As a natural progression of this area of work, we expanded our series of dimers and trimers to those containing only thiophene and furan. We used both 2-thienyl zinc chloride (3.13) and 2-furyl zinc chloride as (3.3) the organometallic precursor. We found no appreciable differences in the quality of the products obtained or in the yields achieved depending on which heterocycle we used as the organometallic.



(3.3) (3.20) (3.21)



(3.3) (3.22) (3.23)



(3.13) (3.24) (3.25)

(i) THF / N_2 atmos. / 50°C / $Pd(PPh_3)_4$.

Scheme III.V

3.4.1 Synthesis

The Pelter *et. al.*[3.3] approach was again used for the synthesis of: 2-(2-furyl) thiophene (3.21); 2,5-di-(2-furyl) thiophene (3.23): and 2,5-di-(2-thienyl) furan (3.25). Scheme III.V details the synthesis of these compounds. Similar to the dimers and trimers prepared previously, these three compounds were prepared by the coupling of a bromoheterocycle and the organometallic in the presence of the palladium catalyst. The first of these, 2-(2-furyl) thiophene (3.21) was prepared in an acceptable yield of 52.9%, as a colourless liquid after distillation from the reaction mixture.

The second, the trimer 2,5-di-(2-furyl) thiophene (3.23), was again prepared by the Pelter *et. al.*[3.3] route. The white solid was obtained in an average yield of 66.9%. The final trimer, 2,5-di-(2-thienyl) furan (3.25), was prepared with a better yield of 77.9%. Again it was prepared by the Pelter *et. al.*[3.3] procedure and separated by careful chromatography on a silica column using hexane:THF (10:3 v/v) as the elutant. No electrochemistry for these monomers was obtained as we decided to concentrate research efforts on the synthesis of soluble polythiophenes as discussed in the next Chapter.

3.5 Conclusions

This Chapter outlines the synthesis and electrochemistry of some mixed heterocyclic dimers and trimers. These monomers were prepared by the organometallic coupling of various heterocyclic moieties. All of the monomers, with the exception of one, were prepared by a palladium catalysed procedure first reported by Pelter *et. al.*[3.3, 3.4] in 1987. This multi-step procedure involved the mono-lithiation of the heterocyclic starting compound at the 2-position. This was then converted to the required organometallic by reaction with zinc chloride. This organometallic heterocycle reacted, in the presence of a tetrakis(triphenylphosphine) palladium catalyst, with a heterocyclic bromide in an average yield of 65%. The one exception to this procedure was 2,5-di-(2-thienyl) pyridine (3.17). This trimer had to be prepared using another catalytic system, which is outlined in Chapter Four.

Some of these dimers and trimers were subjected to electrochemical analysis, to investigate the electropolymerisation and metal binding properties. The first of these electrochemical studies indicates that the monomer 2,6-di-(2-furyl) pyridine (3.12) forms an insulating monolayer layer on the electrode surface and hence prevents any polymerisation, possibly due to a furan-ring opening reaction. The majority of the

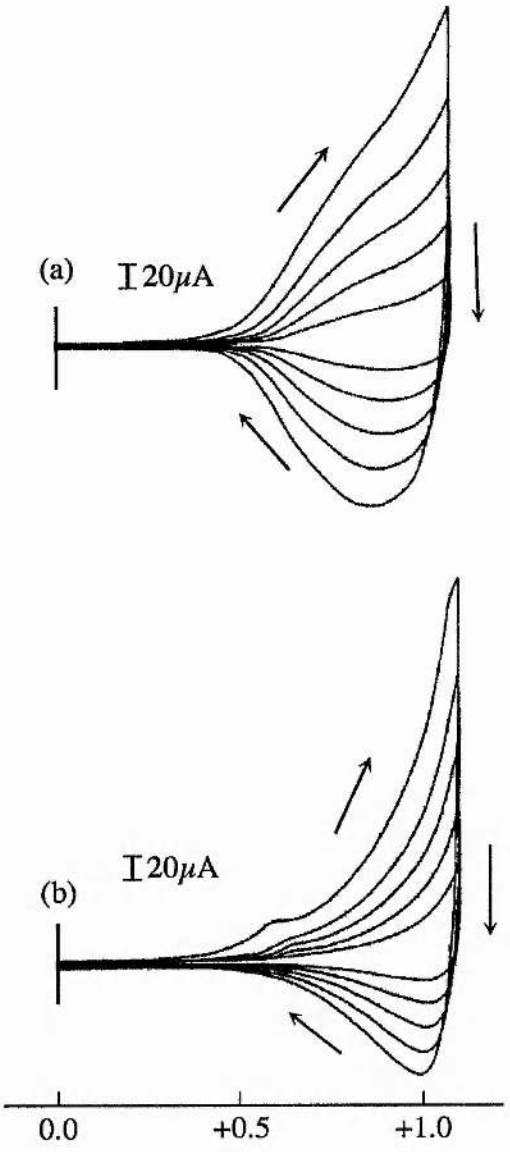
electrochemical investigations involved the three thiophene-pyridine heterocyclic monomers. The first of these 2-(2-thienyl) pyridine (3.14) was easily polymerised and the CV of the polymer revealed some interesting phenomenon. The potential must be swept to -2.5V to show the first set of peaks. The second set of peaks can be obtained only after firstly going negative to -2.5V and then positive to +0.7V. These peaks can be attributed to the oxidation and reduction of the π-excessive thiophene and π-deficient pyridine rings within the polymer chain. This behaviour was not seen at all in the CV's of the two trimers. This is possibly due to the unique alternating charge transfer in the polymer chains or bithiophenes in the 2,5- and 2,6- polymers.

The two remaining thiophene-pyridine trimers were subjected to electropolymerisation and some metal binding experiments. We prepared the two trimers to hopefully investigate any effects of steric hindrance on the metal complexation. The trimer 2,6-di-(2-thienyl) pyridine (3.15) was easily polymerised by sweeping the potential between 0.0V and +2.1V. Any higher potential rapidly led to electrode passivation. The metal binding of the polymer was investigated using a variety of salts: silver; copper; palladium; and ruthenium. Due to the hydrophobic nature of the polymer and its extremely positive conducting regime (>+1.4V) there was little evidence for binding of these metals although it was thought the ruthenium trimeric complex was adsorbed as a monolayer.

The third of these thiophene-pyridine monomers, 2,5-di-(2-thienyl) pyridine (3.17) was again easily electropolymerised with an anodic limit of +1.5V. The polymer doping is much easier than the previous one and this is in line with MO calculations on the relative HOMO energies. Unfortunately, due to lack of time we were unable to carry out a complete study of the metal binding properties of the polymer obtained. We do however show n-doping and possible coordination with copper. We also propose that protonation on the pyridine accounts for the large cathodic current observed and the lack of reproducibility of the results.

Similarly a detailed comparative study of the X-ray structures of the two molecules was prevented. We do however, for the first time, confirm the predicted structure of the monomer 2,5-di-(2-thienyl) pyridine (3.17). We were unable to compare this structure with that of the 2,6-di-(2 thienyl) pyridine (3.15) trimer, as no literature could be found and we were unable to obtain crystals suitable for X-ray analysis. We therefore used similar molecules to give a comparison. The most striking fact is that the molecule is not planar. The thienyl ring attached to the 5-position on the pyridine ring lies at an angle of 7°, whereas at the 2-position the thienyl is almost planer. This is due to the incomplete conjugation along the connecting C-C bond, as noted by the longer bond length, and the steric interaction caused with the S pointing toward a C-H.

A comparison of the cyclic voltammetry of these two polymers does however indicate differences in the conducting properties. Figure 3.19 details the CV for the two polymers in monomer free electrolyte at scan rates 20-100mVs^{-1}. The first striking difference is the width of the peaks for the polymer poly-(2,5-bis-(2-thienyl) pyridine), particularly noticeable when comparing the cathodic peaks. This can easily be attributed to the random nature of the electropolymerisation technique and hence incomplete conjugation of the pyridyl and thienyl moieties within the polymer chain. Another interpretation of sharp redox waves is that they arise from the sudden loss of attractive interactions between redox groups brought about by the introduction of charge on the polymer chain and/or by the ingress of solvent. The second difference is the anomaly of a small anodic shoulder +0.6V, for the polymer poly-(2,6-bis-(2-thienyl) pyridine). This is more difficult to assign, but taking into account the lack of a cathodic peak, it is proposed that this shoulder is due to a small amount of side reaction possibly associated with quaternisation of some of the pyridine rings.



Comparison of the CV's for electrocoupled: (a) 2,5-di-(2-thienyl) pyridine (3.17); and (b) 2,6-di-(2-thienyl) pyridine (3.15). Both recorded in monomer free MeCN / 0.1mM TBAT for scan rates 20-100mV/s.

Figure 3.19

3.6 Experimental

(3.10) Synthesis of 2-(2-furyl) pyridine

In a 500ml, three necked flask equipped with a stirrer a rubber septum and a reflux condenser with nitrogen bubbler was placed furan (10.2g, 0.15moles) and 100ml THF. After cooling to 0°C, n-butyl lithium (93.75ml, 1.6M in hexane, 0.16moles) was added to the stirred solution. The initial red solution of 2-lithiofuran was stirred at 0°C for two hours, after 15 minutes the solution turned a cloudy yellow. In a second 500ml, three necked flask equipped with a stirrer, a rubber septum and a reflux condenser with nitrogen bubbler was placed dry zinc chloride (27.25g, 0.2moles) and 100ml THF. At room temperature, the solution of 2-lithiofuran was added, via a double ended needle, over a period of ten minutes. The resulting solution of 2-furyl zinc chloride was stirred for one hour. In a third 1L, three necked flask equipped with a stirrer, a dropping funnel, a reflux condenser with nitrogen bubbler and a thermometer, was placed 2-bromopyridine (15.8g, 0.1moles) the catalyst (formed in situ - palladium(II) chloride (0.09g, 0.0005moles) and triphenylphosphine (0.52g, 0.0002moles)) and 200ml THF. The mixture was heated to 50°C and the solution of 2-furyl zinc chloride was added dropwise, over a period of ten minutes maintaining the temperature below 60°C. The reaction was heated at 50-60°C for six hours. The cooled solution was poured onto 200ml 0.1M hydrochloric acid and extracted with 100ml diethylether. The aqueous layer was then extracted with 2x100ml diethylether. The combined organic layers were washed with 200ml saturated sodium hydrogen carbonate solution, 2x200ml water, dried and concentrated. The title product was distilled at 89°C / 1.4mmHg, weight 10.5g (72.4%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 8.52 (d, 1H), 7.66 (m, 2H), 7.45 (d, 1H), 7.02 (m, 2H), 6.48 (d of d, 1H) . ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 154.018, 149.893, 149.741, 143.609, 136.894, 122.419, 122.209, 118.842, 108.961

(3.12) Synthesis of 2,6-di-(2-furyl) pyridine

In a 500ml, three necked flask equipped with a stirrer a rubber septum and a reflux condenser with nitrogen bubbler was placed furan (10.2g, 0.15moles) and 100ml THF. After cooling to 0°C, n-butyl lithium (92.4ml, 1.6M in hexane, 0.15moles) was added to the stirred solution. The resulting red solution of 2-lithiofuran was stirred at 0°C for two hours. In a second 500ml, three necked flask equipped with a stirrer, a rubber septum and a reflux condenser with nitrogen bubbler was placed dry zinc chloride (20.1g, 0.15moles) and 100ml THF. At room temperature, the solution of 2-lithiofuran was added, via a double ended needle, over a period of ten minutes. The resulting solution of 2-furyl zinc chloride was stirred for one hour. In a third 1L, three necked flask equipped with a stirrer, a dropping funnel, a reflux condenser with nitrogen bubbler and a thermometer, was placed 2,6-dibromopyridine (12g, 0.05moles) the catalyst (formed in situ - palladium(II) chloride (0.09g, 0.0005moles) and triphenylphosphine (0.52g, 0.0002moles)) and 200ml THF. The mixture was heated to 50°C and the solution of 2-furyl zinc chloride was added dropwise, over ten minutes, maintaining the temperature below 60°C. The reaction was heated at 50-60°C for ten hours. The cooled solution was poured onto 200ml 0.1M hydrochloric acid and extracted with 100ml diethylether. The aqueous layer was extracted with 2x100ml diethylether. The combined organic layers were washed with 200ml saturated sodium hydrogen carbonate solution, 2x200ml water, dried and concentrated. The resulting brown solid was dissolved in 2ml of dichloromethane and chromatographed on a silica column using 40-60 petrol:THF (99:1) as the elutant. The yellow solution was concentrated and recrystallised from petrol to yield the title product as yellow needles, weight 6.37g (60.4%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 7.45-7.22 (m, AB_2 pattern, 3H), 7.29 (d, 2H), 6.96 (d, 2H), 6.29 (d, 2H). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 154.256, 149.654, 143.791, 137.681, 117.187, 112.552, 109.461. MS m/z (relative intensity) 211 (M+ 100), 183 (9), 154 (13), 127 (5), 105 (10). Anal. calc. for $C_{13}H_9NO_2$: C (73.92), H (4.29), N (6.63).

Found: C (72.89), H (4.62), N (6.39).

(3.14) Synthesis of 2-(2-thienyl) pyridine

Preparation was carried out in an identical manner to 2-(2-furyl) pyridine, using thiophene (13.6g, 0.2moles), butyl lithium (125ml, 1.6M in hexane, 0.2moles), dry zinc chloride (34.5g, 0.25moles) and 2-bromo thiophene (24.6g, 0.15moles). The title product was distilled at 96°C / 1.1mmHg, weight 8.2g (56.5%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 8.55 (dd, 1H), 7.69 (m, 2H), 7.59 (dd, 1H), 7.40 (dd, 1H), 7.13 (m, 2H). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 152.004, 149.932, 142.480, 140.020, 130.943, 129.382, 129.042, 127.428, 124.994.

(3.15) Synthesis of 2,6-di-(2-thienyl) pyridine

Preparation was carried out in an identical manner to 2,6-di-(2-furyl) pyridine, using thiophene (16.8g, 0.2moles), n-butyl lithium (125ml, 1.6M in hexane, 0.2moles), dry zinc chloride (27.2g, 0.2moles) and 2-bromopyridine (17.8g, 0.075moles). The title product was recrystallised from ethanol, yellow solid, weight 13.8g (76%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 7.65 (m, 3H), 7.45 (m, 4H), 7.13 (d of d, 2H). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 152.050, 144.803, 137.263, 127.904, 127.718, 124.693, 116.648.

(3.17) Synthesis of 2,5-di-(2-thienyl) pyridine

In a 250ml, three necked flask equipped with a stirrer, a reflux condenser with nitrogen bubbler and a dropping funnel was placed dry magnesium turnings (3g,

0.125moles), a single crystal of iodine and 100ml diethylether. 2-Bromothiophene (18g, 0.11moles) was added dropwise maintaining a gentle reflux, and left to stir at room temperature for one hour. In a second 500ml, three necked flask equipped with a stirrer, a reflux condenser with nitrogen bubbler and a dropping funnel was placed 2,5-dibromopyridine (11.5g, 0.048moles), Ni(dppp)Cl_2 (0.6g, 0.001moles) and 100ml diethylether. After cooling to 0°C the Grignard was added dropwise. Once addition was complete, the adduct was stirred at room temperature for forty hours. The resulting dark brown solution was poured carefully onto 200ml 1M hydrochloric acid. The organic layer was washed with 2x200ml water, dried and concentrated. The brown solid was dissolved in 2ml dichloromethane and chromatographed on a silica column using petrol:THF (99:1 v/v) as the elutant. The yellow solution was concentrated and recrystallised from diethylether to yield the title product as yellow needles, weight 8.85g (76.3%). ^{1}H NMR (200MHz) δ($CDCl_3$) 8.83 (d, 1H), 7.84 (d, 1H), 7.69-7.55 (m, 2H), 7.43-7.31 (m, 3H), 7.12 (m, 2H). ^{13}C NMR (50MHz) δ($CDCl_3$) 151.259, 146.513, 144.423, 140.352, 133.518, 128.534, 128.308, 128.130, 127.689, 125.764, 124.535, 123.866, 118.639.

(3.21) Synthesis of 2-(2-furyl) thiophene

Preparation was carried out in an identical manner to 2-(2-furyl) pyridine, using furan (13.6g, 0.2moles), butyl lithium (125ml, 1.6M in hexane, 0.2moles), dry zinc chloride (34.5g, 0.25moles) and 2-bromo thiophene (24.6g, 0.15moles). The title product was obtained by distillation, weight 11.9g (52.9%). ^{1}H NMR (200MHz) δ($CDCl_3$) 7.4 (m, 1H), 7.2 (m, 2H), 6.9 (m, 1H), 6.5 (m, 2H). ^{13}C NMR (50MHz) δ($CDCl_3$) 150.743, 149.188, 142.723, 130.854, 128.774, 127.447, 118.453, 109.733.

(3.23) Synthesis of 2,5-di-(2-furyl) thiophene

Preparation was carried out in an identical manner to 2,6-di-(2-furyl) pyridine, using furan (20.4g, 0.3moles), butyl lithium (120ml, 2.5M in hexane, 0.3moles), dry zinc chloride (40.8g, 0.3moles) and 2,5-dibromo thiophene (31g, 0.13moles). The title product was thus separated by chromatography, recrystallised from methanol to yield a white solid, m. pt, 60-62°C, weight 18.8g (66.9%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 7.39 (d, 2H), 7.17 (s, 2H), 6.49 (d, 2H), 6.44 (dd, 2H). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 147.196, 142.264, 123.592, 112.346, 112.184, 105.648.

(3.25) Synthesis of 2,5-di-(2-thienyl) furan

Preparation was carried out in an identical manner to 2,6-di-(2-furyl) pyridine, using thiophene (25.2g, 0.3moles), butyl lithium (120ml, 2.5M in hexane, 0.3moles), dry zinc chloride (40.8g, 0.3moles) and 2,5-dibromo furan (29.4g, 0.13moles). The title product was thus separated by chromatography, weight 21.6g (71.6%). ^{1}H NMR (200MHz) $\delta(CDCl_3)$ 7.2 (m, 2H), 7.0 (m, 4H), 6.4 (s, 2H). ^{13}C NMR (50MHz) $\delta(CDCl_3)$ 129.663, 128.774, 127.482, 122.384, 113.456, 109.294.

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3.8 List of Chemicals and Products

3.1 Furan.

3.2 2-Lithiofuran.

3.3 2-Furyl zinc chloride.

3.4 2-Phenylfuran.

3.5 1,4-Dibromobenzene.

3.6 1,4-Di-(2-furyl) benzene.

3.7 1,4-Di-(2-(5-zinc chloride) furyl) benzene.

3.8 Poly-(1,4-bis-(2-furyl) phenyl).

3.9 2-Bromopyridine.

3.10 2-(2-Furyl) pyridine.

3.11 2,6-Dibromopyridine.

3.12 2,6-Di-(2-furyl) pyridine.

3.13 2-Thienyl zinc chloride.

3.14 2-(2-Thienyl) pyridine.

3.15 2,6-Di-(2-thienyl) pyridine.

3.16 2,5-Dibromopyridine.

3.17 2,5-Di-(2-thienyl) pyridine.

3.18 2-Thienyl magnesium bromide.

3.19 Poly-(2,6-bis-(2-thienyl) pyridine).

3.20 2-Bromothiophene.

3.21 2-(2-Furyl) thiophene.

3.22 2,5-Dibromothiophene.

3.23 2,5-Di-(2-furyl) thiophene.

3.24 2,5-Dibromofuran.

3.25 2,5-Di-(2-thienyl) furan.

Chapter Four

Synthesis of Soluble Polythiophenes

4.1 Introduction

Among the numerous conducting polymers prepared, polythiophene has rapidly become the subject of considerable interest. This is mainly due to its ease of synthesis, either chemically or electrochemically. From a theoretical viewpoint, polythiophene has often been considered as a model for the study of charge transport in conducting polymers with a nondegenerate ground state. Another important benefit of polythiophenes, over other conducting polymers, is their high environmental stability - see Chapter One (Table 1). This stability in both the doped and undoped states, together with the structural versatility, have led to multiple developments aimed at applications such as: conductors; electrode materials; and organic semiconductors - this is explored in greater detail in Section 4.2.

Polythiophenes have been considered in several reviews devoted to conducting polymers in general[4.1, 4.2], but there have only been two reviews devoted solely to polythiophenes. The first of these by Tourillon[4.3], was published in 1986 and covered the early developments of the field upto 1985. The second, by Roncali[4.4], covers the considerable progress accomplished in the synthesis of polythiophenes and in the characterisation of their structures, electronic and electrochemical properties since 1985. There have also been several reviews on specific aspects such as: electropolymerisation[4.5]; environmental stability[4.6]; and optical properties[4.7].

The electrochemical synthesis of polythiophene was first reported in 1980[4.8], here 2,2'-dithiophene was used as the monomer. The first electropolymerisation of thiophene appeared two years later[4.9]. Following these initial studies there have been a large number of works devoted to the analysis of the electropolymerisation reaction and to the optimisation of the electrosynthesis conditions. The electrochemistry of polythiophene is dealt with in Chapter Five.

Polythiophene has been known for a long time[4.10], but the origin of the present intensive research into the chemical synthesis of polythiophene is in keeping with the emergence of the widespread interest in conducting polymers in the early 1980's. Thiophene oligomers have been prepared by several methods, some of which have been proposed as adaptable to the preparation of polymers - oligothiophenes have attracted much interest in their own right and Section 4.4 explores these in greater detail. Polythiophenes have been prepared by numerous methods: oxidative coupling of bis-lithiated thiophene monomers[4.11]; plasma polycondensation[4.12]; oxidative polymerisation of dithiophene in the gas phase using AsF_5 under pressure[4.13]; oxidative polymerisation in the liquid phase, initially used for the synthesis of poly(pyrrole), recently has been extended to thiophene[4.14]; and Grignard coupling in the presence of transition metal complexes[4.15, 4.16]. Of these many different methods reported for the chemical synthesis of polythiophenes, a very efficient procedure, and one that is probably the most extensively used, is the Karasch reaction, as modified by Kumada *et. al.*[4.17].

The Kumada[4.17] reaction simply involves the nickel-catalysed coupling of Grignard compounds with bromothiophenes. This is the major scheme employed for our synthesis of oligothiophenes and polythiophenes. The reaction involves the addition of a Grignard to a mixture of organic halide, catalyst and solvent. Stirring at reflux for a number of hours, followed by hydrolysis, yields the coupled products which are further purified by distillation, recrystallisation or

chromatography. The catalyst, [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride, is generally used in a concentration of 0.1-1 mol% of the organic halides. This process is characterised by the fact that the coupling reaction requires only catalytic amounts of the nickel-phosphine complex, proceeds under mild conditions and normally gives high yields. Secondly the organic group is introduced onto the carbon atom to which the halogen had been attached, leading to a product which is isomerically pure.

Unsubstituted polythiophene is insoluble in most common solvents, thus we decided to concentrate our research into finding soluble monomers and polymers. Over the past ten years there has been extensive research into finding soluble, and hence processable polythiophenes. The simplest method of making polythiophene soluble, is by the addition of alkyl side chains to the β-position in the thiophene monomers. This is the method we extensively explore in this Chapter.

4.2 Potential Applications of Polythiophenes

Over the last fifteen years, the considerable research effort invested in conducting polymers has been largely motivated by their numerous potential applications. Polythiophene is one of the simplest conducting polymers to prepare yet it exhibits excellent processing possibilities both in the doped and undoped states - Chapter One (Table 1). These two factors have led to polythiophenes being the most widely investigated conducting polymer. In this Section we discuss some of the potential applications of polythiophenes and give some idea of how close they are to reality. To assist in this discussion these application are divided into three main groups based on: (a) the electrochemical reversibility of the transition between the doped and undoped states; (b) the electronic properties of the neutral semiconducting state; and (c) the electrical properties of the doped conducting state. A detailed review

of all these potential applications is impractical for this report, thus a brief review of each of the three sub-groups is included.

(a) Potential applications based on the electrochemical reversibility of the transition between the doped and undoped states:- Perhaps the most world-wide discussed potential application of all conducting polymers is their use for electrical energy storage in rechargeable batteries. Polythiophenes have been discussed as both the electrolyte and the electrodes. The initial enthusiasm which was based on over-optimistic performance evaluations has now been tempered by the realisation that there are many unresolved problems. Of these problems perhaps the most important are self-discharge and insufficient cycle lives. Overcoming these difficulties is paramount to the development of useful polythiophene based rechargeable batteries. Recent studies of polythiophene cells[4.18] have shown high voltage combined with good energy and power densities, although self-discharge has been a problem[4.19]. Several substituted polythiophenes have been investigated as possible electrode materials[4.20], e.g. solid-state lithium cells involving poly-(ethylene oxide)-$LiClO_4$ electrolytes and polythiophene cathodes have been assembled. These cells unfortunately only operate beyond the phase-transition temperature of the electrolyte (>70°C)[4.21]. More recently, studies based on poly((3-alkyl)thiophenes) have confirmed the influence of the polymer structures on the electrochemical behaviour[4.22].

Another widely discussed application of polythiophenes, is their use in electro-optical systems, such as display devices and electrochromic windows. Initial characterisations revealed good optical contrast and response times ranging from 10 to 300 ms[4.23], and cycle lives of up to 1.2×10^5 charge-discharge cycles have been reported for poly((3-methyl)thiophene) films on bulk platinum electrodes[4.24]. To make these devices useful they will require higher cycle lives. Extensive research is being focused on this area, and cycle lives exceeding 10^7 have recently been

reported for alkyl- and polyether-substituted polythiophenes films operating at 10% of their maximum capacity[4.25].

(b) Potential applications based on the electronic properties of the neutral semiconducting state:- Many devices utilising the electronic properties of the neutral semiconducting state of polythiophene have been postulated. Photoelectrochemical cells based on polythiophene junctions have been discussed[4.26] and more recently photovoltic cells based on electrogenerated polythiophenes have been described. These novel cells show high quantum yields under monochromatic light, but the overall conversion yield under polychromatic light still remains low (0.15%)[4.27]. Although these show great potential for development, the performance of the systems is still largely inferior to those of inorganic semiconductors, thus more research is required to bring these systems out of the laboratory and into our homes.

Molecular electronics, or 'Chemionics', the ability to achieve basic computer functions such as amplification, memory, and logical operations by means of single molecules[4.28] is one of the most exciting areas of modern chemistry. This futuristic concept should overcome the physical limits imposed by inorganic semiconductors in the area of circuit miniaturisation. It is also hoped that this will lead to a new batch of super fast processors as switching speeds of these single molecule devices surpasses that of traditional silicon based devices[4.29]. Polythiophenes have started to be investigated as candidates in this field[4.30], recent examples of polythiophenes being used as molecular wires[4.28], molecular rectifiers[4.31], and in Langmuir-Blodgett films[4.32] have been reported.

(c) Potential applications based on the electrical properties of the doped conducting state:- The conductivity of polythiophene alters greatly upon doping. This effect has been utilised in polythiophene based gas sensors. Exposure of polythiophene films to NO or NO_2 increases the conductivity[4.33], whereas a decrease

in conductivity is shown using H_2S or NH_3[4.34]. This work has also been extended to include a basic radiation detector. In the presence of SF_6 a change in conductivity is observed when a polythiophene film is irradiated with an electron beam[4.35].

Another interesting example of the use of polythiophene is in the protection of the photoelectrodes used in photoelectrochemical solar cells. The semiconducting materials used in these applications are subject to rapid photocorrosion. Traditional insulating polymers limit the corrosion but affect the electronic transfer between the semiconductor and the electrolytic medium. Polythiophene has been postulated as compromise. GaAs photoelectrodes have been stabilised by thin films of polythiophene[4.36]. The only problem with the use of doped polythiophenes, in this application, is that as the polymer losses its dopant the conductivity of the film alters and thus the performance of the solar cells decreases. Stabilisation of the dopant is thus required, this is being investigated using copolymers. Exciting results have been achieved using poly((3-butyl)thiophene) and polypyrrole mixtures[4.37].

4.3 Synthesis of Starting Materials

Before proceeding with the synthesis of oligothiophenes and polythiophenes we were required to prepare some starting materials. Some of these products are commercially available, but as they were expensive, and large quantities were required we decided to prepare them ourselves since their preparations are well documented in literature.

4.3.1 Synthesis of 3-Bromothiophene

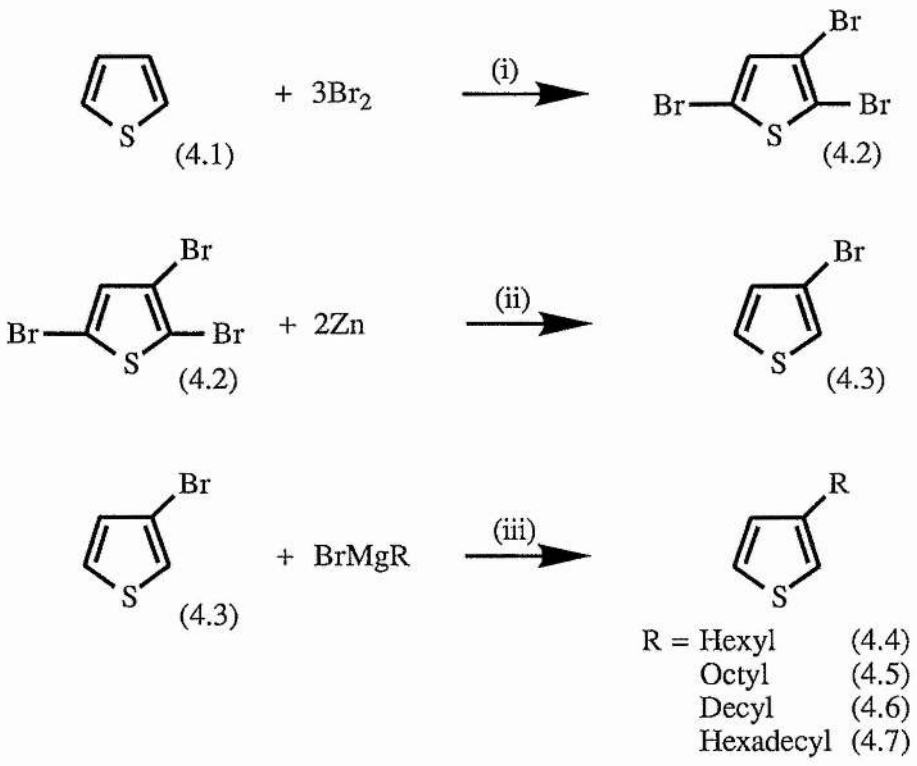
The preparation of 3-bromothiophene (4.3) involved the dropwise addition of

three molar equivalents of bromine to an ice cold solution of thiophene (4.1) in dichloromethane, using the method described by Troyanowsky[4.38]. After work-ups the crude 2,3,5-tribromothiophene (4.2) was then used without further purification in the next step. The reduction of 2,3,5-tribromothiophene (4.2) involves its reaction with powdered zinc in acetic acid. Once the reaction was complete, the required 3-bromothiophene (4.3) was collected by careful fractionation in an acceptable yield of 60.4% as reported by Gronowitz and Raznikiewicz[4.39].

4.3.2 Synthesis of 3-Alkylthiophenes

The use of 3-lithiothiophene in alkylation reactions is restricted. Below 0°C no reaction occurs[4.40], and it is well known[4.41] that above 0°C ring-opening reactions occur, as well as the metal-halogen exchange process[4.42]. The synthesis was thus approached by proceeding with a nickel-catalysed Grignard coupling[4.43] of 3-bromothiophene (4.3) with an alkylmagnesium bromide. 3-Bromothiophene (4.3) is simply prepared by the Gronowitz and Raznikiewicz[4.39] method described in Section 4.3.1 or by a new procedure, which involves the isomerisation of 2-bromothiophene (4.19) on zeolite catalysts[4.44]. This nickel-catalysed Grignard coupling was thus used for the synthesis of 3-hexylthiophene (4.4), 3-octylthiophene (4.5), 3-decylthiophene (4.6) and 3-hexadecylthiophene (4.7) as described in Scheme IV.I.

The 3-alkylthiophenes are prepared using the Karasch reaction, as modified by Kumada *et. al.*[4.17], specifically the experimental details as described by Garnier *et. al.*[4.45]. Here the freshly prepared alkylmagnesium bromide Grignard is added to an ice cold, diethylether solution of 3-bromothiophene (4.3) containing the catalyst [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride. Following acid extraction, washing and drying, distillation yields the required products as colourless liquids in



(i) CH_2Cl_2 / 0°C.

(ii) CH_3COOH / H_2O / reflux.

(iii) Et_2O / Ni(dppp)Cl_2.

Scheme IV.I

yields of: 3-hexylthiophene (4.4), 64.7%; 3-octylthiophene (4.5), 53.1%; 3-decylthiophene (4.6), 68.4%; and 3-hexadecylthiophene (4.7), 62.0%. These 3-alkylthiophenes were then used for the preparation of oligothiophenes and polythiophenes as described later.

4.3.3 Synthesis of Ni(dppp)Cl_2

The catalyst [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride - Ni(dppp)Cl_2, is simply prepared by the method of VanHecka and Horrocks[4.46]. This

involves the addition of a hot solution of nickel(II) chloride hexahydrate in methanol/propanol (1/3 v/v) to a hot stirred solution of 1,3-bis(diphenylphosphino) propane in methanol/propanol (3/5 v/v). The resultant solution was cooled and the reddish brown solid was collected by filtration and dried under vacuum to provide the red complex, Ni(dppp)Cl_2, in almost quantitative yield.

4.4 Synthesis of Oligothiophenes

As a prelude to the synthesis of soluble polythiophenes we decided to investigate the preparation of soluble oligothiophenes containing five and six repeating thiophene units, α-quinquethiophene and α-sexithiophene respectively. The solubility of oligothiophenes, like the parent polymer is poor: α-sexithiophene is partially soluble in trichloromethane ($0.05gL^{-1}$)[4.47]. As described previously the major method for obtaining soluble polymers is the addition of solublizing alkyl side chains in the β-position on the thiophene rings. This method is explored for the preparation of our soluble oligothiophenes. These oligothiophenes serve as well defined models for refined studies and a more accurate definition of the properties of the conducting polymers[4.48]. Oligothiophenes, similar to polythiophenes, have found many potential applications. This again is due to their ease of synthesis, their ability to be processed into thin, homogeneous films with various degrees of molecular orientation and the possibility to 'tune' the electronic properties by alteration of the chain length or the addition of subtituents on either free α- or β-positions. The remainder of this Section details three potential applications of oligothiophenes: (a) semiconducting materials; (b) optical light modulators; and (c) biologically active compounds.

(a) Semiconducting materials:- Along with the development of LED's[4.49], the homogeneous, defect-free molecular structure of a thin layer of α-sexithiophene has

been successfully used to build an all organic field effect transistor[4.50]. This new device not only uses an organic polymer as the semiconducting material, but for the first time, the whole device is made up of various polymeric materials, except the contacts which are metallic. Along with α-sexithiophene as the semiconducting layer, cyanoethylpullulan was used as the insulating layer and poly(parabanic acid) resin was used as the film support. Contrary to the intrinsic stiffness shown by inorganic semiconductors, the all organic structure possesses the very interesting and useful property of mechanical flexibility. Results have shown that after considerable twisting and bending no noticeable modification of the semiconducting characteristics were observed.

(b) Optical light modulators:- Data transfer in optical processing systems performing Fourier-transform-type operations is essentially limited by the response time of the input and output transducers, but could in principle approach the frequency of light. These light modulators are two-dimensional input devices aimed at fully utilising the potential speeds and parallelism capabilities of light. They can be considered as the building blocks of image and beam processors[4.51]. Conventionally, the active recording material can be a liquid crystal[4.52], a photorefractive crystal[4.53], a multi-quantum-well semiconductor[4.54] or a silver-halide film[4.55]. Fichou and co-workers[4.56] recently reported the development of an ultra fast optical converter using α-sexithiophene as the photochromic material. This new device, compared with traditional incoherent-to-coherent optical converters[4.57], can improve the speeds and spatial resolution of the image processing by two orders magnitude while having the same exposure sensitivity.

(c) Biologically active compounds:- Oligothiophene are important compounds for biological studies. Plants belonging to the family *Compositae* contain several mono-, bi- and terthiophenes which exhibit numerous important biological properties[4.58]. As an example, α-terthiophene exhibits photoenhanced actives against

nematodes[4.59], micro-organisms, in particular *E. Coli*[4.60], algae[4.61], human erythrocytes[4.62], insect eggs[4.63] and larvae[4.64]. It has also be shown to be effective as a skin pigment generator[4.65] and as a seed germination inhibitor[4.66]. The biological activity of larger unsubstituded oligomers is much less common. This is probably due to their insolubility in biological medium. The addition of side chains to enable solubility, will allow the investigation of the biological activity of these larger oligothiophenes.

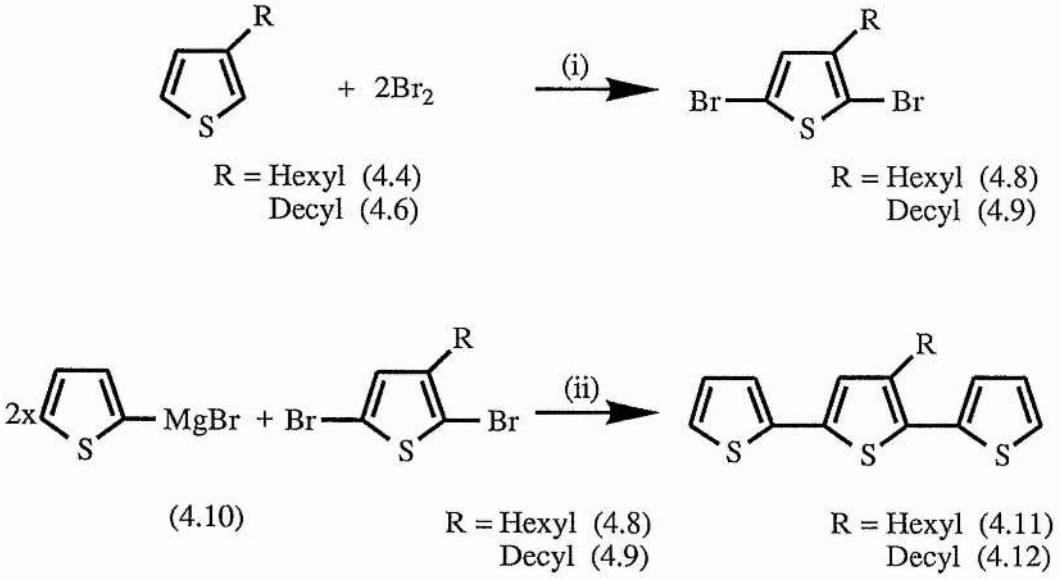
4.4.1 Synthesis of Sexithiophenes

A simple approach to the preparation of a soluble α-sexithiophene is the dimerisation of soluble trimers. An example of a soluble trimer is 3'-alkyl-2,2';5',2"-terthiophene, whose preparation is described in Scheme IV.II. The synthesis follows a two step procedure. Firstly, dibromination of 3-alkylthiophene gives quantitative yields of 2,5-dibromo-3-hexylthiophene (4.8) and 2,5-dibromo-3-decylthiophene (4.9). Secondly, the Karasch reaction, as modified by Kumada *et. al.*[4.17] is again employed. The Grignard reactions produces no dimeric intermediates. In fact, the first substitution on the dibromothiophene activates the second one, which accounts for the relatively high yields of purified product 3'-hexyl-2,2';5',2"-terthiophene (4.11) 80.0% and 3'-decyl-2,2';5',2"-terthiophene (4.12) 82.8%. This is a testament of the great efficiency of the Kumada modification.

The dimerisation of the prepared trimers 3'-hexyl-2,2';5',2"-terthiophene (4.11) and 3'-decyl-2,2';5',2"-terthiophene (4.12) is detailed in Scheme IV.III. The homocoupling of the lithiated derivative of the terthiophenes is by means of a cupric chloride coupling that yields the required β',β''''-dihexyl-2,2';5',2";5",2"';5"',2"";5"",2""'-sexithiophene (4.13) and β',β""-didecyl-2,2';5',2";5",2"';5"',2"";5"",2""'-sexithiophene (4.14) in yields of 43.4% and

48.5% respectively. Any longer oligomers, arising from bis-lithiated terthiophenes and unreacted terthiophenes were successfully removed using chromatography on silica gel.

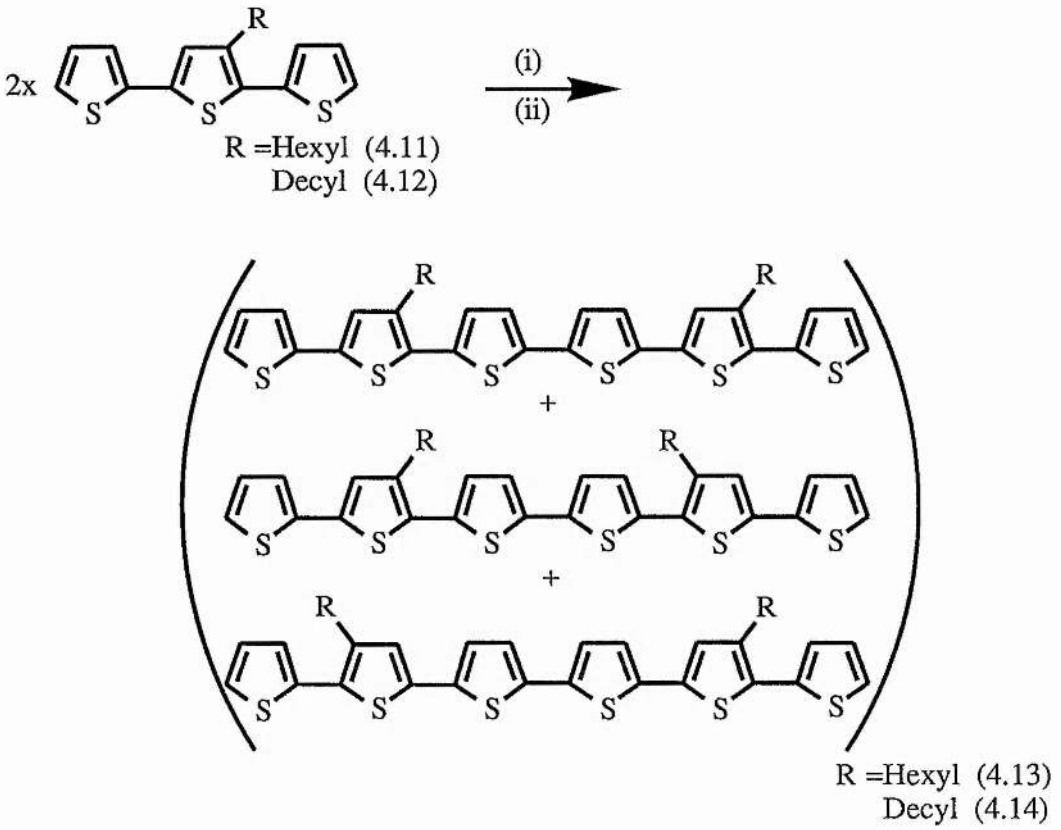
It can be seen that this method successfully prepares α-sexithiophenes, but unfortunately the dimerisation reaction yields a mixture of three isomers, as outlined in Scheme IV.III. We therefore had to find methods of preparing soluble oligothiophenes of defined configuration. Although we did not explore this for the synthesis of α-sexithiophenes we have investigated this topic further for the synthesis of α-quinquethiophenes as described below in Section 4.4.2, and it was assumed that these techniques would prove as successful for the α-sexithiophenes as they were for the α-quinquethiophenes.



(i) CH_2Cl_2 / 0°C.

(ii) Et_2O / Ni(dppp)Cl_2.

Scheme IV.II



(i) ^{n}BuLi / THF / -10°C.

(ii) $CuCl_2$ / 20°C.

Scheme IV.III

4.4.2 Synthesis of Quinquethiophenes

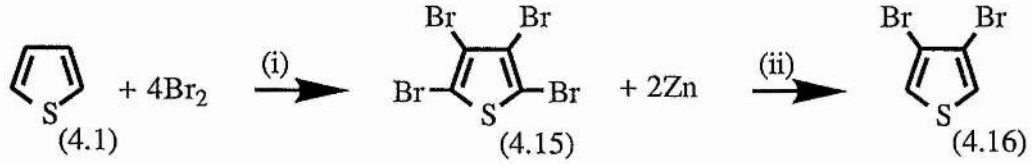
As mentioned above the successful synthesis of the α-sexithiophenes was marred only by the fact that the exact configuration of the resultant products was not known. In this Section we discuss methods which yield α-quinquethiophenes with two alkyl side chains of known configuration. The first of these methods overcomes the conformational problem by simply placing both the alkyl chains on the same thiophene, the third one in the chain to yield 3",4"-dihexyl-2,2';5',2";5",2'";

5''',2''''-pentathiophene (4.23). This method could have been used to prepare α-sexithiophenes with four identical alkyl chains on the second and fifth thiophenes. Similar work has been reported Kanatzidis *et. al.*[4.67], they used butyl side chains to prepare α-sexithiophenes for X-ray diffraction work.

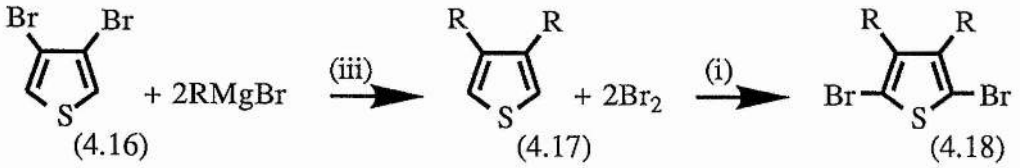
The preparation of the 3'',4''-dihexyl-2,2';5',2'';5'',2''';5''',2''''-pentathiophene (4.23) follows the synthetic route as postulated by Benz and LeGoff[4.68]. Scheme IV.IV outlines the reaction which yields the required pentamer as a red powder, in a yield of 32.7%. This complex procedure involves the synthesis of two separate precursor molecules. The first of these precursor molecules, 2,5-dibromo-3,4-dihexylthiophene (4.18), is prepared in a four step procedure starting from thiophene, using many of the procedures discussed previously.

The second of these precursor molecules, 5-bromo-2,2'-dithiophene (4.21) was simply prepared by a two step method. Firstly, the Grignard coupling of 2-thienyl magnesium bromide (4.10) and 2-bromothiophene (4.19) afforded 2,2'-dithiophene (4.20) as a colourless liquid, which discoloured overnight. Further distillations were stored in the dark which delayed the onset of the discolouration. The monobromination of this 2,2'-dithiophene (4.20) was simply achieved by the addition of bromine. The required 5-bromo-2,2'-dithiophene (4.21) was separated by careful distillation from unreacted starting material and the dibrominated product, as a colourless liquid in an average yield of 54.3%. Although not the most efficient procedure it was sufficient for the small quantities that were required.

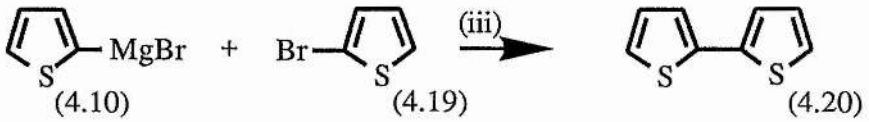
A superior method for the synthesis of α-bromo-oligothiophenes has recently been reported by Bäuerle *et. al.*[4.69]. This method, contrary to those previously reported[4.70], produced the required α-bromo-oligothiophenes in acceptable yields, and with a high degree of isomeric control. This method, like others[4.71], uses *N*-bromosuccinimide (NBS), but this time dimethylformamide is used as the solvent and



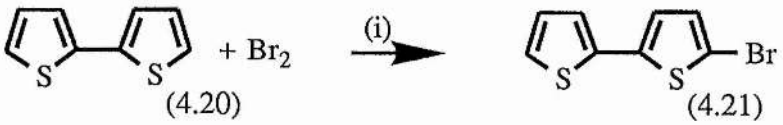
(4.1) (4.15) (4.16)



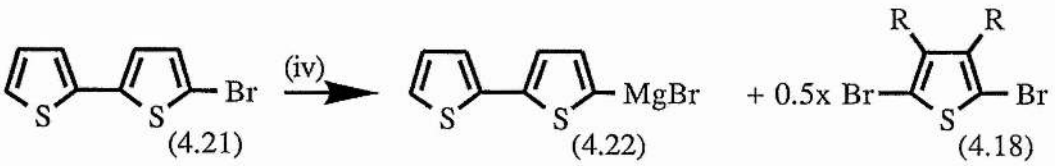
(4.16) (4.17) (4.18)



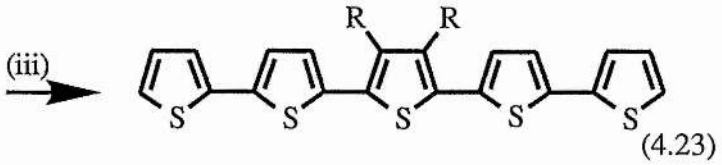
(4.10) (4.19) (4.20)



(4.20) (4.21)



(4.21) (4.22) (4.18)



(4.23)

R = Hexyl

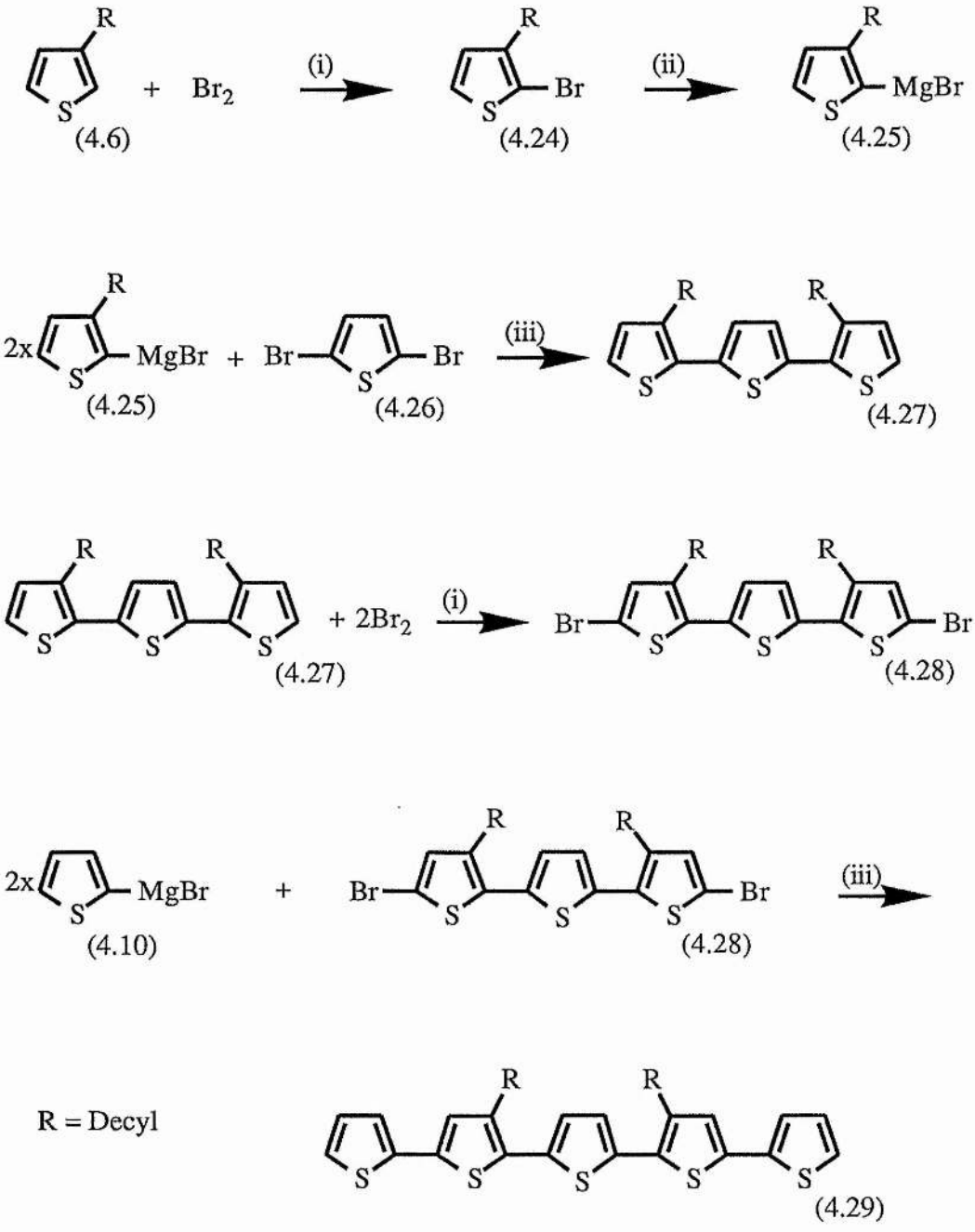
(i) CH_2Cl_2 / 0°C.

(ii) CH_3COOH / H_2O / reflux.

(iii) Et_2O / Ni(dppp)Cl_2.

(iv) Mg / Et_2O / reflux.

Scheme IV.IV



(i) CH_2Cl_2 / 0°C.

(ii) Mg / Et_2O / reflux.

(iii) Et_2O / Ni(dppp)Cl_2.

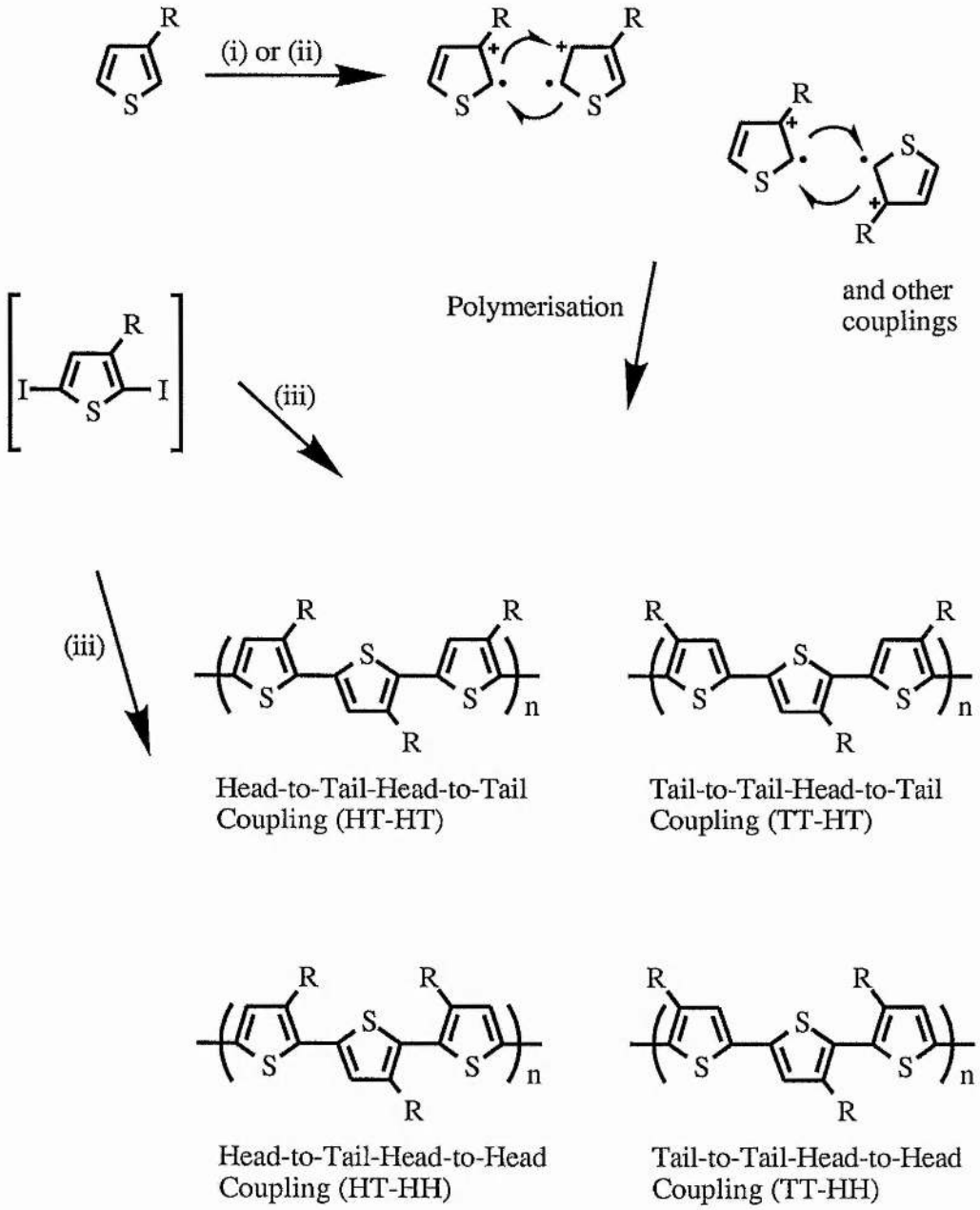
Scheme IV.V

the temperature is -20°C. The new method produces, in some cases, as little as 5% of the α,α-dibrominated-oligothiophene, compared to other which give up to 50%[4.70].

The second α-quinquethiophene prepared matches more closely with our work on α-sexithiophenes, in that the two alkyl side chains are located on different thiophenes but this time the exact conformation is known. This is achieved by carefully planning the synthesis to eliminate the random dimerisation technique as used in the synthesis of our α-sexithiophenes and by others[4.72]. Scheme IV.V details our multi-step process. Firstly, we monobrominate 3-decylthiophene (4.6) at the 2-position. Bromination at the 2-position is preferred[4.73], for reasons explored further in Section 4.5. The 2-bromo-3-decylthiophene (4.24) is converted to the Grignard reagent and two equivalents react with 2,5-dibromothiophene (4.26) to give the trimer 3,3''-didecyl-2,2';5',2''-terthiophene (4.27). The trimer is then dibrominated at the two free α-positions to yield 5,5''-dibromo-3,3''-didecyl-2,2';5',2''-terthiophene (4.28) in quantitative amounts. The final stage involves the nickel-catalysed Grignard coupling[4.17], which after purification by chromatography, yields 62.4% of the desired final product 4',3'''-didecyl-2,2';5',2'';5'',2''';5''',2''''-pentathiophene (4.29) as a reddish brown powder.

4.5 Synthesis of Poly((3-alkyl)thiophenes)

Recent reports[4.74, 4.75] have outlined synthetic pathways for the chemical synthesis of structurally homogeneous poly((3-alkyl)thiophenes). In comparison to other procedures[4.76, 4.77] this new technique allows for regiochemical control and produces, for the first time, structurally homogeneous poly((3-alkyl)thiophenes). In this context, the term 'structurally homogeneous' refers to a regiochemically well-defined polymer that contains almost exclusively head-to-tail coupling. Similar to classical polyacetylene, the standard synthetic methods used to prepare poly((3-

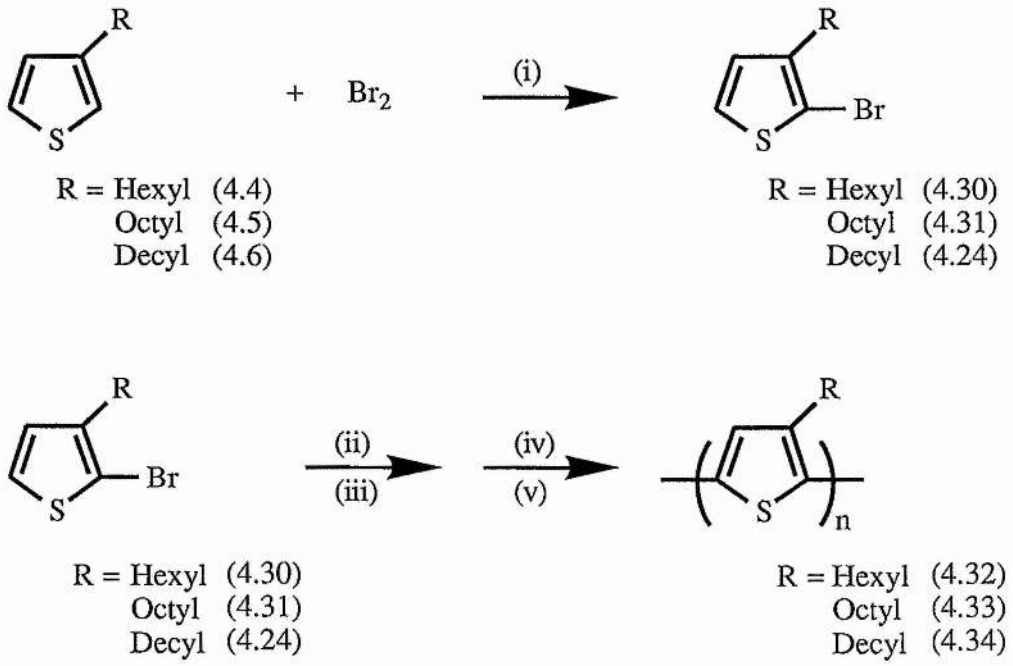


(i) $FeCl_3$.

(ii) $-e^-$ at Pt.

(iii) Mg / Ni^{2+} cat' polymerisation.

Figure 4.1



(i) CH_3COOH / H_2O / reflux.

(ii) LDA / THF / -40°C.

(iii) $MgBr_2OEt_2$ / -60°C to -40°C.

(iv) -40°C to -5°C.

(v) $Ni(dppp)Cl_2$ / -5°C to 25°C.

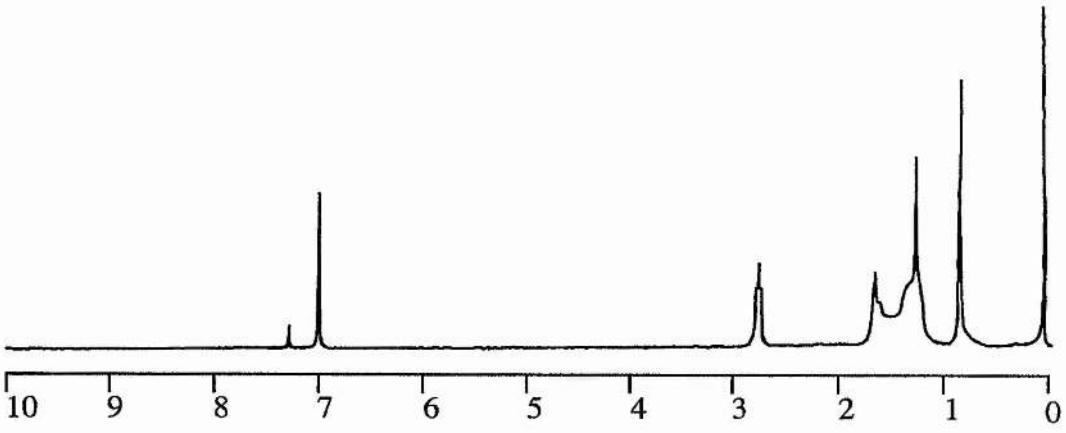
Scheme IV.VI

alkyl)thiophene), as outlined in Figure 4.1, generate a large number of defects due to the random couplings at the 2,5-positions on the thiophene rings[4.78]. Due to the steric interactions between alkyl chains, these structures must contain a large number of thiophene rings that are twisted far out of conjugation and hence a decrease in the polymer conductivity is observed. A structurally homogeneous head-to-tail arrangement would therefore improve the material's electrical and optical properties[4.79].

This new method involves a complex four step, one pot procedure, starting from 2-bromo-3-alkylthiophenes - Scheme IV.VI. Contrary to the regiospecific bromination of 3-methylthiophene with NBS, the bromination of 3-alkylthiophenes at the 2-position requires bromine in acetic acid, as reported by Gronowitz[4.73]. This simple bromination procedure was successfully employed for the preparation of: 2-bromo-3-hexylthiophene (4.30); 2-bromo-3-octylthiophene (4.31); and 2-bromo-3-decylthiophene (4.24) in yields of: 39.3%; 37.8%; and 39.6% respectively.

The polymerisation proceeds via the metallation of the 2-bromo-3-alkylthiophene selectively at the 5-position. This is followed by trapping of the formed 2-bromo-3-alkyl-5-lithiothiophenes with magnesium bromide etherate to afford the target Grignard monomer. Subsequent treatment with the catalyst, [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride, leads to the regiochemically defined head-to-tail coupled poly((3-alkyl)thiophenes). The resultant brown solids were purified by precipitation from methanol to afford red solids which were further purified by Soxhlet extraction, using a number of solvents. Methanol and hexane extraction removed any oligomers and impurities, while dichloromethane dissolved the polymer out of the catalytic mixture. These complex purification procedures produced the required polymers: poly((3-hexyl)thiophene) (4.32); poly((3-octyl)thiophene) (4.33); and poly((3-decyl)thiophene) (4.34) as red powders in yields of: 43.9%; 52.6%; and 47.7% respectively.

Sato and Morii[4.78, 4.80] deduced through a series of ^{1}H NMR studies that 54% of their electrogenerated poly((3-dodecyl)thiophene) consisted of head-to-tail couplings. Therefore in terms of the conducting properties of the polymer, almost half of the couplings are defects. In their study they reported four singlets in the aromatic region. These singlets can be clearly attributed to the protons at the 4-position on the thiophene ring, each peak resulting from a different type of trimeric sequence of: HT-HT (δ6.98); HT-HH (δ7.00); TT-HT (δ7.02); and TT-HH (δ7.05)



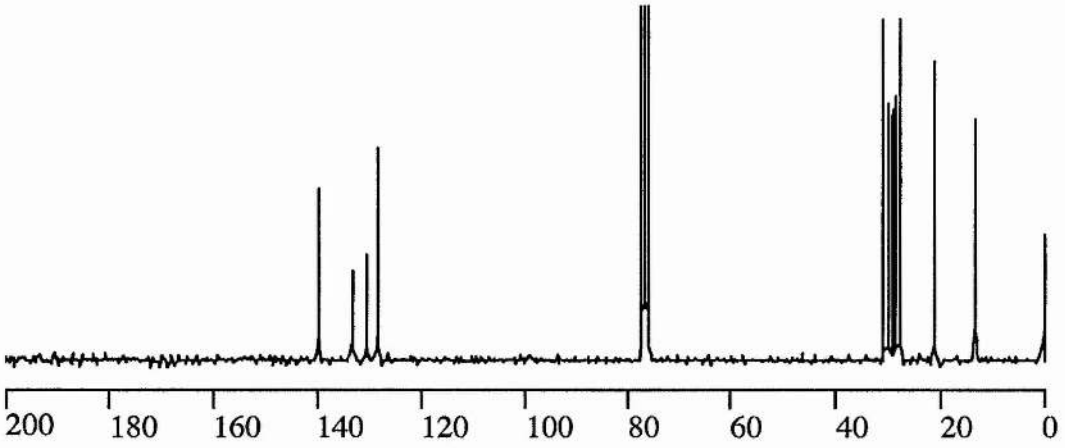
^{1}H NMR (200MHz) $\delta(CDCl_3)$ spectra for poly((3-octyl)thiophene) (4.33).

Figure 4.2

linked thiophene rings - Figure 4.1. In comparison our poly((3-alkyl)thiophenes) prepared by the new method, afforded strikingly clear ^{1}H spectra, which showed only one singlet in the aromatic region.

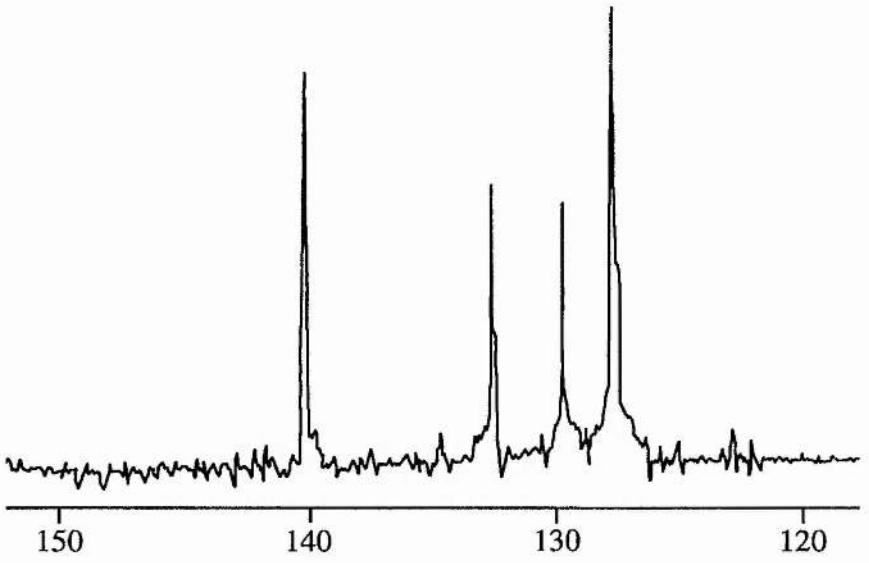
As an example, Figure 4.2 and Figure 4.3 show the full proton and carbon spectra of poly((3-octyl)thiophene) (4.33). Figure 4.4 details the expanded methylene and aromatic regions of the ^{1}H NMR spectra of poly((3-octyl)thiophene) (4.33) prepared by the new method. Included as a comparison the extended regions of poly((3-octyl)thiophene) (4.33) prepared by the simple $FeCl_3$ are included[4.81]. As can be clearly seen the polymer prepared by the new method yields a singlet, in the aromatic region (δ6.98) - Figure 4.4(a). The ^{1}H NMR of poly((3-octyl)thiophene) prepared by the $FeCl_3$ method gives a broad peak which upon closer inspection shows four singlets - Figure 4.4(c). These four singlets match the results for the four trimeric sequence as reported by Sato and Morii, and as detailed in Figure 4.1.

The ^{13}C NMR spectra reinforces that our poly((3-alkyl)thiophenes) contains a



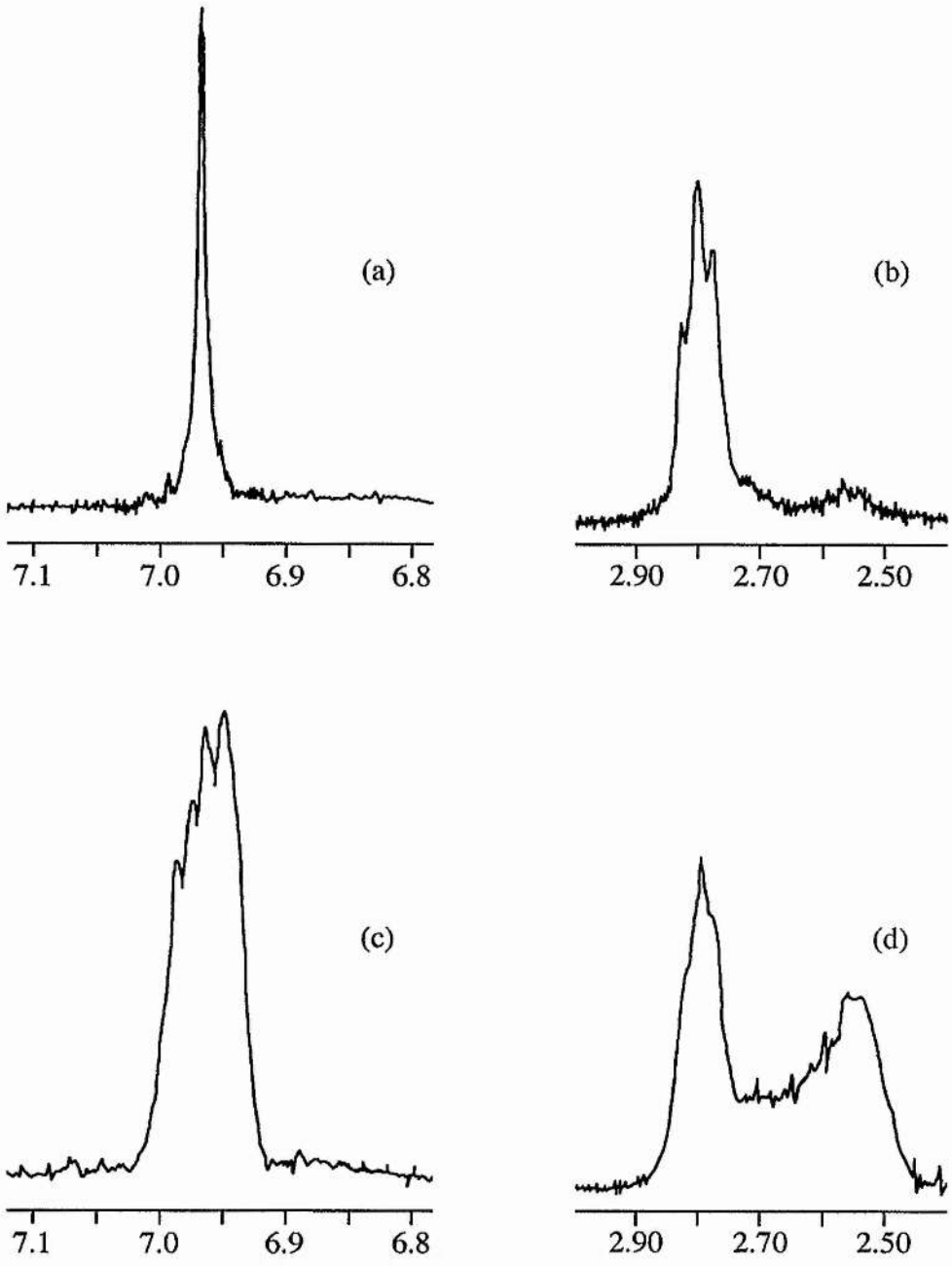
^{13}C NMR (50MHz) $\delta(CDCl_3)$ spectra for poly((3-octyl)thiophene) (4.33).

Figure 4.3



^{13}C NMR (50MHz) $\delta(CDCl_3)$ spectra for poly((3-octyl)thiophene) (4.33), extended aromatic region δ(152-118) by our method.

Figure 4.5



^{1}H NMR (200MHz) δ($CDCl_3$) spectra of poly((3-octyl)thiophene) (4.33): (a) expanded aromatic region δ(7.12-6.79) by our method; (b) expanded methylene region δ(3.00-2.40) by our method; (c) expanded aromatic region δ(7.12-6.79) by $FeCl_3$ method; and (d) expanded methylene region δ(3.00-2.40) by $FeCl_3$ method.

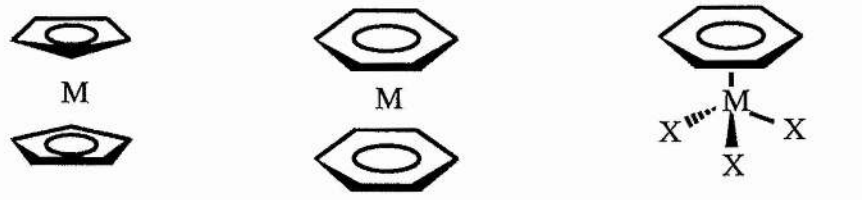
Figure 4.4

high proportion of head-to-tail couplings. The ^{13}C NMR spectra, Figure 4.3, shows only eight absorptions in the alkyl region and exclusively four absorptions in the aromatic region. These four predominant absorptions can be attributed to the carbons on one regiochemically defined thiophene ring. Other reports[4.82, 4.83] of poly((3-octyl)thiophene) (4.33) prepared by the $FeCl_3$ method show sixteen resonances that represent the four isomers as detailed in Figure 4.1. The expanded ^{13}C NMR spectra of the aromatic region δ(152-118) of our poly((3-octyl)thiophene) (4.33) is shown in Figure 4.5. A small number of peaks, which are barely distinguishable from the base line, are present. These resonances are most likely to be attributed to the scrambling of the starting material, 2-bromo-3-octyl-5-lithiothiophene.

4.6 Introduction of Metal Binding Sites

To continue the successful research on soluble polythiophenes we decided to expanded our range of monomers to those which may enable metal binding. This was simply achieved by the addition of aryl sites at various positions, on the precursor monomers. This Section includes my initial investigations and my ideas for some polymers containing metal binding sites.

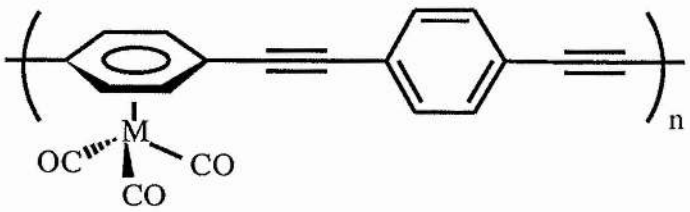
Aryl rings have been shown to selectively bind to metals[4.84]. Figure 4.6 details some of the classical complexes. Recent reports have outlined metal complexation directly onto the backbone of a polymer chain[4.85] - Figure 4.7. Our initial approach to achieving polythiophenes with aryl groups was to place them at the 3-position on the parent thiophene monomer, either at the end of the alkyl chain or directly conjugated with the thiophene ring, i.e. pendant aryl rings. The second approach was to include the aryl moiety directly in the polymer chain. Both these ideas proved synthetically sound and some interesting precursor molecules were prepared. Figure 4.8 outlines some potential polymers containing pendant complexes.



M = Fe, Ru | M = Cr, Ru | M = Cr, Mo, W; X = CO, PPh_3, NO

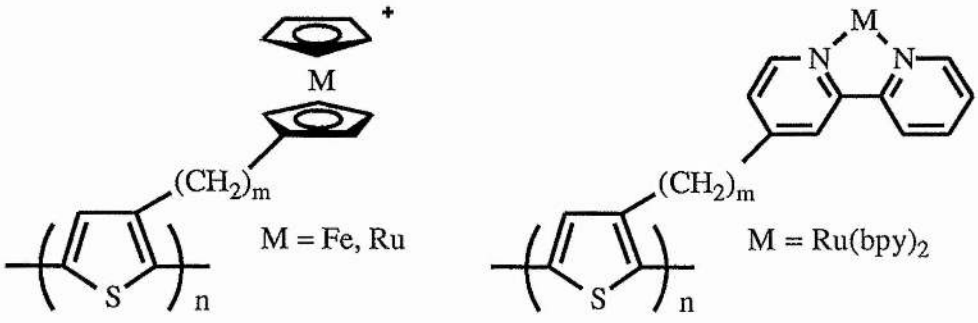
Examples of aryl-metal complexes.

Figure 4.6



Example of metal complexation directly onto the polymer backbone[4.86].

Figure 4.7



Examples of polythiophenes containing pendant metal complexes.

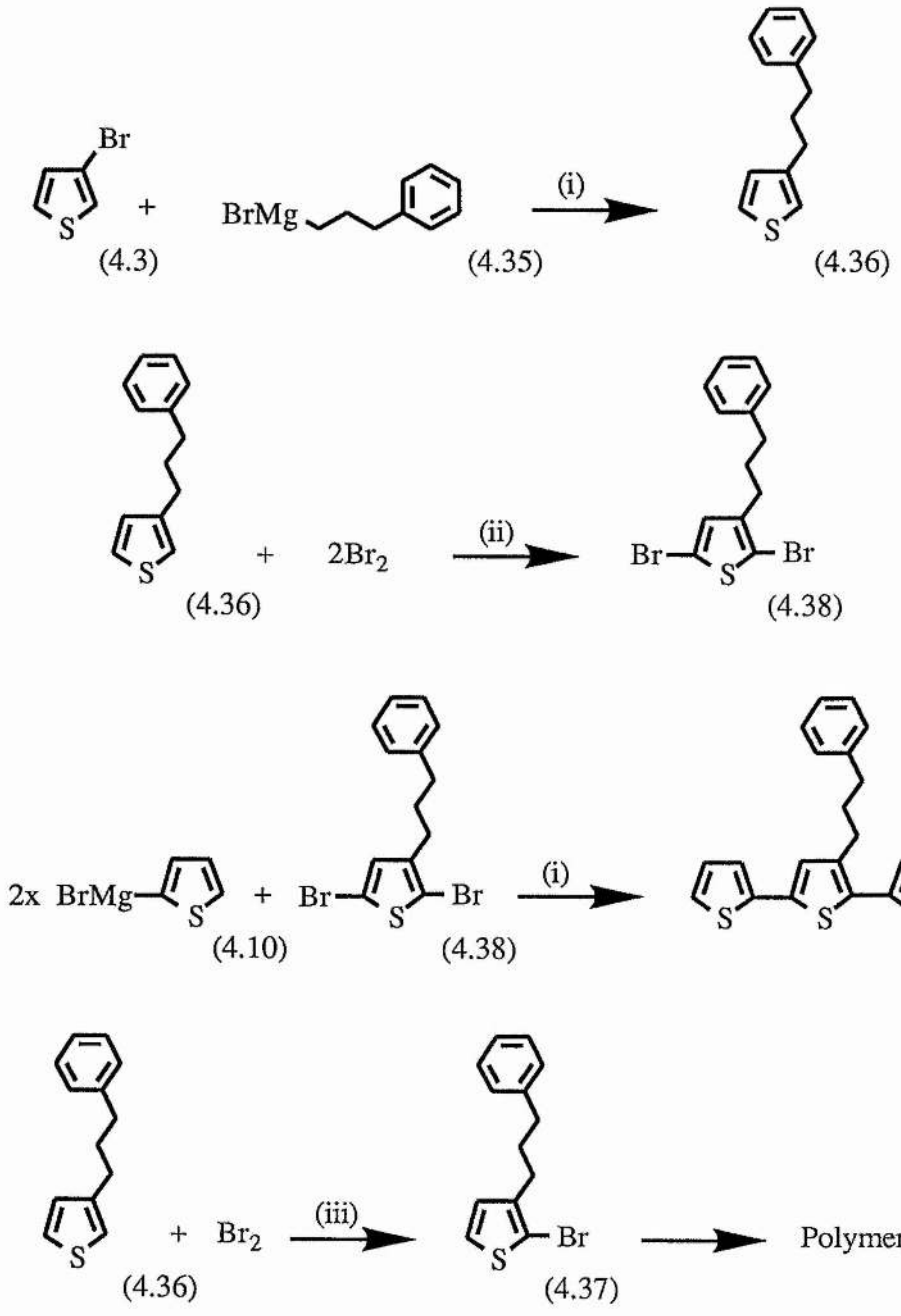
Figure 4.8

4.6.1 Polythiophenes Containing Pendant Aryl Rings

Our initial investigations into this area began with the addition of a ω-phenylalkyl chain at the 3-position on the thiophene monomer. This was achieved by using 1-bromo-3-phenylpropane as the bromoalkyl in the preparation of the Grignard, as detailed in Scheme IV.VII. The reaction proceeded as described for the straight chain alkyls - Section 4.3.2, to yield the colourless liquid in an acceptable yield of 62.0%. The freshly prepared 3-(3-phenylpropyl)thiophene (4.36) was then subjected to mono- and di-bromination using the simple bromination techniques described previously. The mono-bromination yielded 2-bromo-3-(3-phenylpropyl)thiophene (4.37) as a liquid in an average yield of 44.0%. This mono-brominated thiophene was prepared to continue the series of polythiophenes as detailed in Section 4.5.

The di-bromination of 3-(3-phenylpropyl)thiophene (4.36), was simply achieved by the addition, at 0°C, of two equivalents of bromine. This yielded the required 2,5-dibromo-3-(3-phenylpropyl)thiophene (4.38) in a excellent yield of 84.4%. This dibrominated thiophene was then converted to the trimer, 3'-(3-phenylpropyl)-2,2';5',2"-terthiophene (4.39), by the Grignard coupling with two equivalents of thienyl magnesium bromide (4.10) as detailed previously in Section 4.4.1, and outlined in Scheme IV.VII. This trimer was to be dimerised and the α-sexithiophene investigated for its electrochemical behaviour and metal binding properties. Unfortunately, constraints prevented full investigations from being carried out.

To continue with this line of research it would be useful to prepare 3-(ω-bromoalkyl)thiophenes (4.40) thus enabling the Grignard coupling to the end of the alkyl chain and hence the addition of group to this terminal position. Bäuerle *et. al.*[4.86] recently reported a synthetic pathway which leads to the required

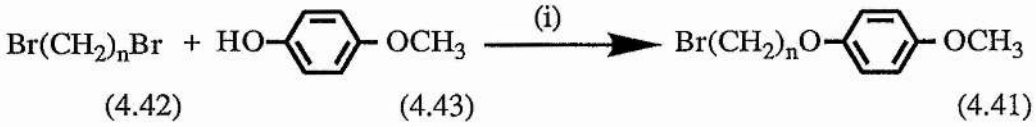


(i) Et_2O / $Ni(dppp)Cl_2$.

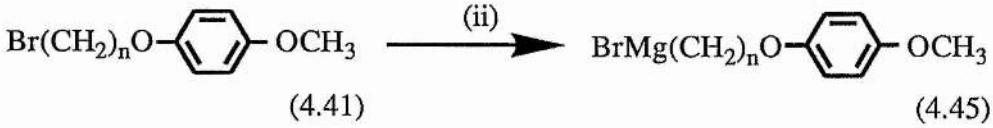
(ii) CH_2Cl_2 / 0°C.

(iii) CH_3COOH / H_2O / reflux.

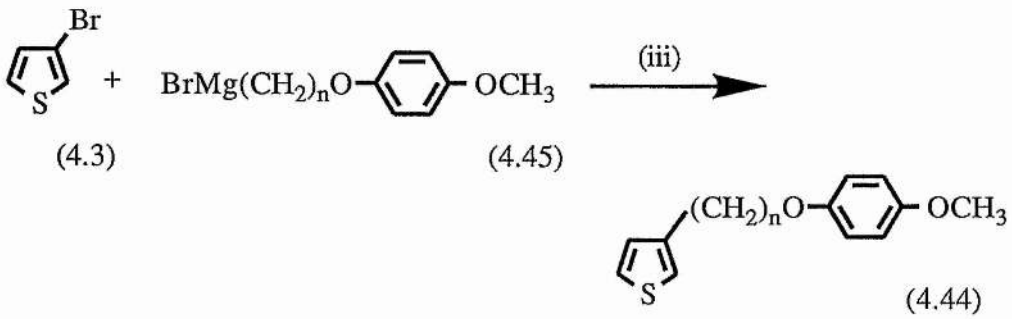
Scheme IV.VII



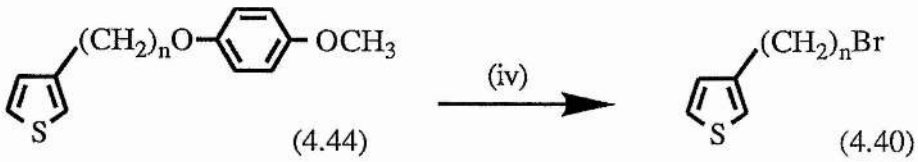
(4.42) (4.43) (4.41)



(4.41) (4.45)



(4.3) (4.45) (4.44)



(4.44) (4.40)

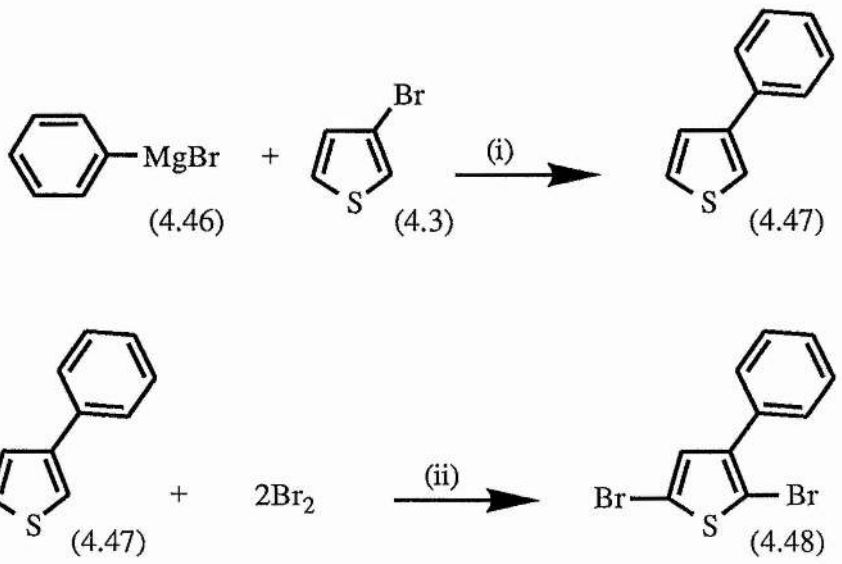
(i) KOH / MeOH / reflux.

(ii) Mg / Et_2O / reflux.

(iii) Et_2O / Ni(dppp)Cl_2.

(iv) HBr / Ac_2O / 100°C.

Scheme IV.VIII



(i) Et_2O / $Ni(dppp)Cl_2$.

(ii) CH_2Cl_2 / 0°C.

Scheme IV.IX

3-(ω-bromoalkyl)thiophene (4.40). This is achieved by using ω-(*p*-methoxyphenoxy) alkyl bromides (4.41), which are easily prepared from α,ω-dihaloalkanes (4.42) and hydroquinone monomethyl ether (4.43)[4.87] - Scheme IV.VIII. This readily reacts with magnesium to afford the Grignard which under goes a catalysed coupling with 3-bromothiophene (4.3). The deprotection of the 3-[ω-(*p*-methoxyphenoxy)alkyl] thiophene (4.44) is effected using hydrogen bromide in acetic anhydride to yield the required 3-(ω-haloalkyl)thiophenes (4.40) - Scheme IV.VIII. Although these experiments were not carried out, they have been included here because they would have been the next line of attack in the preparation of soluble polythiophenes with pendant metal binding sites.

The direct conjugation of a phenyl moiety onto a thiophene monomer is easily achieved using the standard nickel-catalysed Grignard reaction of phenyl magnesium

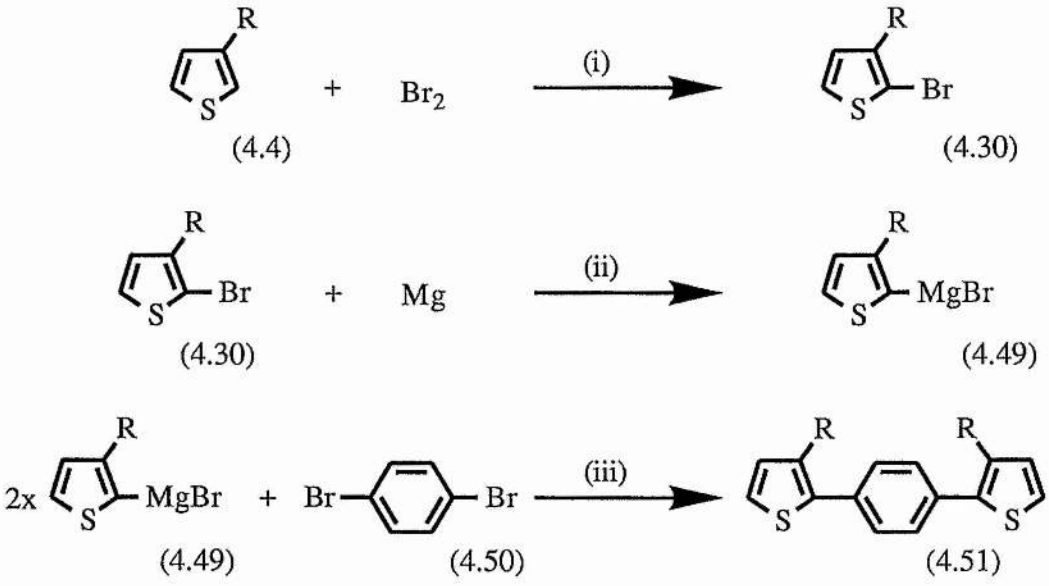
bromide (4.46) and 3-bromothiophene (4.3) - Scheme IV.IX. This yielded the required adduct, 3-phenylthiophene (4.47), as a colourless liquid in an average yield of 62%. Unfortunately, due to the lack of time we were unable to prepare any oligomers or polymers from this adduct. The dibrominated compound, 2,5-dibromo-3-phenylthiophene (4.48), was however prepared as a first step to the oligomerisation reaction.

4.6.2 Towards Mixed Aryl, Thienyl Polymers

The inclusion of aryl rings within the polymer chains should be easily achieved as the nickel-catalysed Grignard reaction works for the coupling of 2-bromothiophene (4.19) and bromobenzene[4.88]. A number of preliminary studies were undertaken toward the synthesis of soluble polymer chains containing both aryl and thienyl moieties. The first line of approach was the simple nickel-catalysed Grignard coupling of two equivalents 2-(3-hexyl)thienyl magnesium bromide (4.49) and 1,4-dibromobenzene (4.50). Scheme IV.X details the preparation of 1,4-di-(2-(3-hexyl)thienyl)benzene (4.51). This trimer was prepared in a yield of 63.2%. The colourless liquid was to be used as the precursor monomer for the preparation of a heterogeneous mixed aryl, thienyl polymer. This polymer, due to its careful design, should have high conductivity. This would be due to the limited steric interaction of the alkyl chain, and hence less tortional twisting in the polymer chain.

4.7 Discussion

It has now been twenty-five years, since the initial reports of the conducting properties of normally insulating polymers, were first published. In the ensuing years many new materials have been prepared and this originally obscure field of chemistry



R = Hexyl

(i) CH_2Cl_2 / 0°C.

(ii) Et_2O / reflux.

(iii) Et_2O / $Ni(dppp)Cl_2$.

Scheme IV.X

has now firmly established itself. Of the many conducting polymers that have been reported, polythiophene has rapidly become the one of the most widely studied. This is mainly due to its ease of syntheses, either chemically or electrochemically, and their enormous potential for development into practical applications. This Chapter detailed my investigations into chemical methods of preparing these simple, yet potentially extremely useful polymers.

Of the numerous published methods of chemically preparing polythiophenes, one that has rapidly risen above the others, in terms of ease of use and purity of products obtained, is the nickel-catalysed coupling of Grignards with bromothiophenes - the Karasch reaction, as modified by Kumada[4.17]. This method

has been successfully used for the preparation of various coupled heterocyclic products. It has proven particularly useful for the preparation of oligothiophenes and polythiophenes and is the major reaction scheme used for our synthetic pathways.

Before proceeding with the preparation of soluble polythiophenes, initial investigations into methods of obtaining greater solubility were undertaken. These primary studies took the form of preparing oligothiophenes, with five or six repeating thiophene units. We successfully prepared four oligothiophenes, two α-sexithiophenes and two α-quinquethiophenes. Their synthesis involved procedures which could easily be extended to the preparation of polythiophenes. The solubility of these oligothiophenes was simply achieved by the inclusion of alkyl chains at the β-position on the thiophene monomer. The longer the alkyl chain or the greater number of chains, increased the solubility of the products. The two α-sexithiophenes were simply prepared by a cupric-catalysed dimerisation of soluble trimers. This procedure could be expanded, by dibrominating the precursor monomer then using the cupric-catalysed coupling method, it is conceivable that soluble polythiophenes should be obtained. This was not carried out as this procedure would lead to a non-regiochemically defined polymer, due to the random nature of the cupric-catalysed coupling reaction. To over come this random conformation problem, other methods were investigated.

The other two oligothiophenes were prepared as isomerically pure compounds. This was achieved by carefully planning the synthetic pathways. Although this led to multi-step procedures, the compounds prepared gave an insight into the properties and techniques required for the synthesis of soluble polythiophenes. The first of these novel α-quinquethiophenes overcomes the conformational problem by placing the two alkyl chains on the same thiophene unit. Other groups have reported that two alkyl chain positioned at the 3- and 4-positions

may cause straining of the aromatic thiophene structure. Our second α-quinquethiophene, similar to the α-sexithiophenes, contains two alkyl chains on different thiophene units. This time, however, the exact conformation was known. Although the conductivity measurements of these oligothiophenes was not carried out, it is conceivable that the length of the alkyl chains might affect the coplanar nature of the thiophene rings. These two oligothiophenes could again probably undergo the dimerisation technique and yield polythiophenes. This was not undertaken as the design of these oligothiophenes led to products which possessed problems of steric interaction between the alkyl chains.

To overcome these conformational and steric problems it was decided to concentrate research efforts into the preparation of a regiochemically well-defined polymers which contain only one alkyl chain on each thiophene moiety. To complicate things a little further, these alkyl chains also had to be aligned so as to eliminate steric hindrance and hence minimise the twisting of the thiophene rings out of coplanarity. These two defects have been shown to lead to polymers which exhibit lower electric and optical properties. Taking these factors into account we concentrated our research into the preparation of poly((3-alkyl)thiophenes). This seemingly straight-forward polymer is extremely difficult to prepare using standard chemical or electrochemical processes. All the classical synthetic procedures yield products with a large number of defects due to their random coupling nature. Recent reports outlined a synthetic methology which overcomes the random nature by simply designing the monomer to include both components of the Grignard reaction and an alkyl chain in an exact conformation. The subsequent treatment of these well defined monomers, with the nickel catalyst, leads to a regiochemically defined, defect free, poly((3-alkyl)thiophenes).

The regiochemical conformation of these new poly((3-alkyl)thiophenes) was confirmed by a series of proton and carbon NMR studies. The ^{1}H NMR spectra

clearly shows a well defined singlet in the aromatic region, this is due to a single trimeric conformation within the polymer chain structure. In comparison to other reported studies, which show four singlets in this region due to the four trimeric conformations, it can be assumed that our polymers contain the required defect free homogeneous structure. Similarly, only one methylene triplet indicates a high degree of conformational control in polymer structure. This analysis was confirmed, and reinforced, by the ^{13}C NMR spectra which clearly showed only four predominant absorptions in the aromatic region. These proton and carbon NMR studies clearly shows that this new method proved very successful in the preparation of structurally homogeneous poly((3-alkyl)thiophenes), that contained almost exclusively head-to-tail couplings. This will enable, for the first time, the investigation of defect free structures which should show improvements in the optical and electronic properties.

The remainder of this Chapter deals with primary investigations into soluble polythiophenes which contain aryl rings. The aryl rings were to be used as sites, either pendant or within the polymer backbone, for metal complexation. Studies by other groups have shown that metals such as chromium, molybdenum and iron, can complex with aryl rings within polymer chains. Although no metal complexation studies were undertaken, a number of starting materials for the formation of oligothiophenes and polythiophenes with potential metal binding sites were prepared.

4.8 Summary

In conclusion, these investigations into the preparation of soluble oligothiophenes and polythiophenes have given a clear insight into the many different synthetic methods postulated for their preparation. These methods were successfully used for the preparation of four oligothiophenes, two of which are novel. These four oligothiophenes all had inherent conformational problems, due to their synthetic

design. These steric problems would cause twisting of the thiophene rings out of their natural coplanar structure. This twisting would ultimately lead to a lower conductivity than would be predicted for the thiophene structure. These conformation problems were overcome in the preparation of poly((3-alkyl)thiophenes) by planning a synthetic procedure that eliminated the random nature of the normal coupling reactions. We successfully prepared three polythiophenes which had, on average 95% of the required head-to-tail couplings. The conformation of these soluble well defined poly((3-alkyl)thiophenes) was confirmed by proton and carbon NMR studies. The electrochemistry of these oligothiophenes and polythiophenes was investigated and is described in Chapter Five.

4.9 Experimental

(4.3) Synthesis of 3-bromothiophene

In a 2L, three necked flask equipped with a stirrer, a dropping funnel and an outlet for the hydrogen bromide evolved was placed thiophene (84g, 1mole) and 500ml of dichloromethane. The flask was then cooled in an ice-bath and bromine (480g, 3moles) was added dropwise to the stirred solution over a period of four hours. The mixture was left to stir overnight and then poured onto 500ml 2M sodium hydroxide. The organic layer was collected and washed with 3x500ml water, dried and concentrated. The crude 2,3,5-tribromothiophene was then used without any further purification. In a second 2L, three necked flask equipped with an efficient mechanical stirrer, a reflux condenser and a dropping funnel was placed zinc dust (185g, 2.83moles), 300ml of glacial acetic acid and 300ml water. The stirred mixture was heated to reflux and then the heat removed. The crude 2,3,5-tribromothiophene was then added dropwise maintaining a steady reflux. The addition was complete in twenty minutes. Heat was then applied and the mixture refluxed for a further hour.

The condenser was then arranged for downward distillation and the mixture was distilled until no more organic substance distilled with the water. The heavier organic layer was separated, washed with 100ml saturated sodium hydrogen carbonate solution, 2x100ml water and dried. Fractionation yielded a 9.8g forerun b.pt. 78-159°C consisting of thiophene and 3-bromothiophene. The title compound was distilled at 159-161°C, weight 98.5g (60.4%). ^{1}H-NMR (200 MHz) $\delta(CDCl_3)$ 7.30 (m, 2H), 7.05 (m, 1H). ^{13}C-NMR (50 MHz) $\delta(CDCl_3)$ 130.471, 127.179, 123.246, 110.581.

Synthesis of [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride

In a 500ml conical flask was placed nickel(II) chloride hexahydrate (1.66g, 0.007moles), 60ml propanol and 20ml methanol. In a second 250ml conical flask was placed 1,3-bis(diphenylphosphino)propane (2.57g, 0.0062moles), 50ml propanol and 30ml methanol. Once both the solids were dissolved, the latter was added to the former and resultant mixture was stirred at room temperature for two hours. The resultant reddish brown solid was collected by filtration and dried to yield to title compound, weight 3.1g (92.3%). Anal. Calc. for $C_{27}H_{26}Cl_2P_2Ni$: C (59.88), H (4.83). Found: C (59.76), H (4.89).

(4.4) Synthesis of 3-hexylthiophene

In a 1L, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed dry magnesium turnings (18g, 0.75moles), a single crystal of iodine and 150ml diethylether. A solution of 1-bromohexane (123.8g, 0.75moles) in 100ml diethylether was placed in the dropping funnel. A small aliquot, 25ml of the 1-bromohexane solution was run into

the reaction flask. Once the reaction had started (ether boiling and turbid colour) the flask was cooled in an ice-bath and the remainder of the 1-bromohexane solution was added over a ten minute period maintaining a gentle reflux. The flask was then removed from the ice-bath and left to stir at room temperature for two hours. In a second 1L, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed 3-bromothiophene (114.1g, 0.7moles), [1,3-bis-(diphenylphosphino)propane]-nickel(II) chloride (0.97g, 0.0018moles) and 150ml diethylether. After cooling in an ice-bath the Grignard solution was added dropwise. Once the addition was complete the resulting adduct was allowed to warm to room temperature and left to stir for sixty-eight hours. The resulting dark brown solution was poured carefully onto 200ml 1M hydrochloric acid solution. The organic layer was washed with 3x200ml water, dried and concentrated. The title compound was distilled at 77°C / 1mm Hg, weight 76.2g (64.7%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.28 (m, 1H), 7.00 (m, 2H), 2.74 (t, 2H), 1.75 (p, 2H), 1.43 (m, 6H), 1.02 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 143.736, 128.847, 125.652, 120.426, 32.4847, 31.3140, 31.0410, 29.8056, 23.4124, 14.8294.

(4.5) Synthesis of 3-octylthiophene

Preparation was carried in an identical manner to 3-hexylthiophene, using dry magnesium turnings (6.7g, 0.28moles), 1-bromooctane (48.2g, 0.25moles), 3-bromothiophene (39g, 0.24moles) and [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (0.27g, 0.0005moles). The title product was distilled at 129-130°C / 2.7mm Hg, weight 25g (53%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.28 (m, 1H), 6.95 (m, 2H), 2.65 (t, 2H), 1.65 (p, 2H), 1.32 (m, 10H), 0.92 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 143.787, 128.808, 125.539, 120.262, 32.4261, 31.1098, 30.6206, 29.9836, 29.8966, 29.8198, 23.2203, 14.6656.

(4.6) Synthesis of 3-decylthiophene

Preparation was carried in an identical manner to 3-hexylthiophene, using dry magnesium turnings (6g, 0.25moles), 1-bromodecane (50.8g, 0.23moles), 3-bromothiophene (32.6g, 0.2moles) and [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (0.27g, 0.0005moles). The title product was distilled at 160°C / 2mm Hg, weight 30.6g (68.4%). ^{1}H-NMR (200MHz) δ($CDCl_3$) 7.30 (m, 1H), 7.00 (m, 2H), 2.72 (t, 2H), 1.70 (p, 2H), 1.40 (m, 14H), 1.00 (t, 3H). ^{13}C-NMR (50MHz) δ($CDCl_3$) 143.742, 128.798, 125.573, 120.316, 32.5770, 31.2230, 30.9217, 30.3900, 30.3423, 30.2950, 30.1554, 30.0200, 23.3558, 14.7647.

(4.7) Synthesis of 3-hexadecylthiophene

Preparation was carried in an identical manner to 3-hexylthiophene, using dry magnesium turnings (10g, 0.42moles), 1-bromohexadecane (122g, 0.40moles), 3-bromothiophene (57g, 0.35moles) and [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (0.27g, 0.0005moles). The title product was separated by distillation, weight 66.9g (62.0%). ^{1}H-NMR (200MHz) δ($CDCl_3$) 7.31 (m, 1H), 6.97 (m, 2H), 2.70 (t, 2H), 1.73 (p, 2H), 1.37 (m, 26H), 0.98 (t, 3H). ^{13}C-NMR (50MHz) δ($CDCl_3$) 143.763, 128.817, 125.589, 120.325, 32.4986, 31.3257, 31.2879, 31.2230, 30.9217, 30.3900, 30.2950, 30.1554, 30.0200, 29.9463, 29.9356, 29.9303, 29.9012, 29.8635, 23.3894, 14.6543.

(4.8) Synthesis of 2,5-dibromo-3-hexylthiophene

In a 500ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser was placed 3-hexylthiophene (16.8g, 0.1moles) and 100ml

dichloromethane. Bromine (32g, 0.2moles) was added dropwise. Once the addition was complete the resulting solution was left to stir for twenty hours at room temperature, then poured onto 200ml 1M sodium hydroxide. The organic layer was washed with 3x200ml water, dried and concentrated. The crude product was then purified on a silica-gel column eluting with hexane. Unreacted 3-hexylthiophene and monobromo-3-hexylthiophene were eluted first. The title compound was thus separated as a colourless liquid, weight 29.8g (91.4%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 6.90 (s, 1H), 2.64 (t, 2H), 1.52 (p, 2H), 1.32 (m, 6H), 0.90 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 142.010, 132.800, 109.999, 108.595, 32.0783, 31.3706, 29.4761, 29.0050, 23.1617, 14.6838.

(4.9) Synthesis of 2,5-dibromo-3-decylthiophene

Preparation was carried in an identical manner to 2,5-dibromo-3-hexylthiophene, using 3-decylthiophene (11.2g, 0.05moles) and bromine (16.0g, 0.1moles). The title product was thus separated by chromatography, as a colourless liquid, weight 16.8g (88%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 6.90 (s, 1H), 2.65 (t, 2H), 1.50 (p, 2H), 1.34 (m, 14H), 0.90 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 141.896, 132.462, 110.032, 108.731, 32.1732, 31.5935, 30.7402, 30.5934, 30.3219, 30.1042, 29.9493, 29.8525, 23.4527, 14.8394.

(4.11) Synthesis of 3'-hexyl-2,2';5',2''-terthiophene

In a 250ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed dry magnesium turnings (3g, 0.125moles), a single crystal of iodine and 30ml diethylether. A solution of 2-bromothiophene (19.6g, 0.12moles) in 50ml diethylether was placed in the

dropping funnel. 10ml of the 2-bromothiophene solution was run into the reaction flask. Once the reaction had started (ether boiling and turbid colour) the remainder of the 2-bromothiophene solution was added over a ten minute period, maintaining gentle reflux. Once addition was complete the Grignard solution was left to stir at room temperature for two hours. In a second 500ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed 2,5-dibromo-3-hexylthiophene (17.9g, 0.054moles), [1,3-bis(diphenyl phosphino) propane]-nickel(II) chloride (0.16g, 0.0003moles) and 50ml diethylether. After cooling, in an ice-bath, the Grignard solution was added dropwise. Once the addition was complete the resulting adduct was allowed to warm to room temperature and left to stir for sixteen hours. The resulting dark brown solution was poured carefully onto 100ml 1M hydrochloric acid solution. The organic layer was washed with 3x100ml water, dried and concentrated. The crude product was purified on a silica-gel column eluting with hexane. The title product was thus separated, as a colourless liquid, weight 14.3g (80.0%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.23 (m, 5H), 7.02 (m, 2H), 2.68 (t, 2H), 1.52 (p, 2H), 1.33 (m, 6H), 0.92 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 142.066, 137.958, 135.453, 134.167, 128.295, 127.374, 125.389, 124.852, 124.269, 116.343, 110.039, 108.640, 32.1147, 31.4009, 29.5125, 29.0474, 23.2041, 14.7202.

(4.12) Synthesis of 3'-decyl-2,2';5',2''-terthiophene

Preparation was carried in an identical manner to 3'-hexyl-2,2';5',2''-terthiophene, using dry magnesium turnings (1.8g, 0.075moles), 2-bromothiophene (11.4g, 0.07moles), 2,5-dibromo-3-decylthiophene (11.45g, 0.03moles) and [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (0.16g, 0.0003moles). The title product was thus separated by chromatography, as a colourless liquid, weight 9.64g (82.7%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.30 (m, 5H), 7.05 (m, 2H), 2.71

(t, 2H), 1.58 (p, 2H), 1.28 (m, 14H), 0.92 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 140.294, 137.674, 136.032, 135.185, 129.749, 128.102, 127.364, 126.392, 125.837, 124.283, 124.032, 123.740, 32.1935, 30.5934, 30.3942, 30.1843, 30.0328, 29.9932, 29.8428, 29.7293, 23.1048, 14.7843.

(4.13) Synthesis of β',β''''-dihexyl-2,2';5',2'';5'',2''';5''',2'''';5'''',2'''''-sexithiophene

In a 250ml, three necked flask equipped with a stirrer, a reflux condenser with nitrogen bubbler and a rubber septum was placed 3'-hexyl-2,2';5',2"-terthiophene (3.96g, 0.012moles) in 50ml THF. The solution was cooled in an ice-salt bath and butyl lithium (4.8ml, 2.5M in hexane, 0.012moles) was added. The resulting solution was left to stir for thirty minutes and anhydrous copper(II) chloride (3g, 0.022moles) was added. The mixture was left to stir at for ten hours. 50ml of water was added and the mixture stirred for a further thirty minutes. The organic solvents were evaporated and the aqueous layer extracted with 2x30ml dichloromethane. The combined organic layers were washed with 2x25ml water, dried and concentrated. The crude product was purified on a silica-gel column eluting with hexane. The title product was thus separated a red powder, weight 1.72g (43.4%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.10 (m, 12H), 2.65 (m, 4H), 1.55 (m, 4H), 1.10 (s, 12H), 0.90 (t, 6H).

(4.14) Synthesis of β',β''''-didecyl-2,2';5',2'';5'',2''';5''',2'''';5'''',2'''''-sexithiophene

Preparation was carried out in an identical manner to β',β''''-dihexyl-2,2';5',2"; 5",2'"; 5'",2'''"; 5'''",2'''''-sexithiophene, using 3'-decyl-2,2';5',2"-

terthiophene (4.66g, 0.012moles), butyl lithium (4.8ml, 2.5M in hexane, 0.012moles) and anhydrous copper(II) chloride (3g, 0.022moles). The title product was thus separated by chromatography, as a red solid, weight 2.25g (48.5%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.05 (m, 12H), 2.70 (m, 4H), 1.50 (m, 4H), 1.05 (s, 28H), 0.95 (t, 6H).

(4.16) Synthesis of 3,4-dibromothiophene

In a 500ml, three necked flask equipped with a stirrer, a dropping funnel and an outlet for the hydrogen bromide evolved was placed thiophene (25.2g, 0.3moles) and 200ml of dichloromethane. The flask was then cooled in an ice-bath and bromine (192g, 1.2moles) was added dropwise to the stirred solution over a period of two hours. The mixture was left to stir overnight and then poured onto 300ml 1M sodium hydroxide. The organic layer was collected and washed with 3x200ml water, dried and concentrated. The crude 2,3,4,5-tetrabromothiophene was then used without any further purification. In a second 1L, three necked flask equipped with an efficient mechanical stirrer, a reflux condenser and a dropping funnel was placed zinc dust (45.4g, 0.7moles), 150ml of glacial acetic acid and 150ml water. The stirred mixture was heated to reflux and then the heat removed. The crude 2,3,4,5-tetrabromothiophene was then added dropwise maintaining a steady reflux. The addition was complete in thirty minutes. Heat was then applied and the mixture refluxed for a further two hours. The condenser was then arranged for downward distillation and the mixture was distilled until no more organic substance distilled with the water. The heavier organic layer was separated, washed with 100ml sat. sodium hydrogen carbonate solution, 3x100ml water and dried. Fractionation yielded a 4.5g forerun b.pt. 78-220°C consisting of a mixture of brominated thiophenes. The title compound was distilled at 220-222°C, weight 45.1g (62.1%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.24 (s, 2H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 123.527, 114.023.

(4.17) Synthesis of 3,4-dihexylthiophene

In a 250ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed dry magnesium turnings (8.2g, 0.34moles), a single crystal of iodine and 70ml diethylether. A solution of 1-bromohexane (52.8g, 0.32moles) in 50ml diethylether was placed in the dropping funnel. A small aliquot, 10ml of the 1-bromohexane solution was run into the reaction flask. Once the reaction had started (ether boiling and turbid colour) the flask was cooled in an ice-bath and the remainder of the 1-bromohexane solution was added over a twenty minute period maintaining a gentle reflux. The flask was then removed from the ice-bath and left to stir at room temperature for three hours. In a second 500ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed 3,4-dibromothiophene (36.3g, 0.15moles), [1,3-bis-(diphenylphosphino)propane]-nickel(II) chloride (0.27g, 0.0005moles) and 150ml diethylether. After cooling in an ice-bath the Grignard solution was added dropwise. Once the addition was complete the resulting adduct was allowed to warm to room temperature and left to stir overnight. The resulting dark brown solution was poured carefully onto 200ml 1M hydrochloric acid solution. The organic layer was washed with 3x200ml water, dried and concentrated. The title compound was distilled at 88°C / 2.4mm Hg, weight 16.3g (43.1%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.25 (s, 2H), 2.73 (t, 4H), 1.71 (p, 4H), 1.36 (m, 12H), 0.98 (t, 6H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 124.283, 114.455, 32.4584, 30.2383, 30.1979, 30.1979, 23.2324, 14.6777.

(4.18) Synthesis of 2,5-dibromo-3,4-dihexylthiophene

Preparation was carried in an identical manner to 2,5-dibromo-3-hexylthiophene, using 3,4-dihexylthiophene (15.1g, 0.06moles) and bromine

(19.2g, 0.12moles). The title product was thus separated by chromatography, as a colourless liquid, weight 22.4g (91.1%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 2.76 (t, 4H), 1.69 (p, 4H), 1.35 (m, 12H), 1.03 (t, 6H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 140.271, 111.698, 32.7610, 30.8193, 30.4286, 30.2187, 23.4091, 13.9873.

(4.20) Synthesis of 2,2'-dithiophene

In a 500ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed dry magnesium turnings (7.2g, 0.3moles), a single crystal of iodine and 100ml diethylether. A solution of 2-bromothiophene (47.3g, 0.29moles) in 100ml diethylether was placed in the dropping funnel. 10ml of the 2-bromothiophene solution was run into the reaction flask. Once the reaction had started (ether boiling and turbid colour) the remainder of the 2-bromothiophene solution was added over a twenty minute period, maintaining gentle reflux. Once addition was complete the Grignard was left to stir at room temperature for one hour. In a second 1L, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed 2-bromothiophene (45.6g, 0.28moles), [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (0.27g, 0.0005moles) and 100ml diethylether. After cooling, in an ice-bath, the Grignard was added dropwise. Once the addition was complete the resulting adduct was allowed to warm to room temperature and left to stir for forty-eight hours. The resulting dark brown solution was poured carefully onto 200ml 1M hydrochloric acid. The organic layer was washed with 3x100ml water, dried and concentrated. The title product was distilled at 81°C / 1.1mm Hg, weight 29.7g (63.8%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.2 (d, 2H), 7.0 (d, 2H), 6.8 (d, 1H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 130.420, 128.228, 127.563, 112.763.

(4.21) Synthesis of 5-bromo-2,2'-dithiophene

In a 250ml, three necked flask equipped with a stirrer, a dropping funnel and an outlet for the hydrogen bromide evolved was placed 2,2'-dithiophene (28.2g, 0.17moles) and 100ml dichloromethane. The flask was cooled in an ice-bath and bromine (27.2g, 0.17moles) was added dropwise to the stirred solution over a period of forty minutes. The mixture was left to stir for four hours and then poured onto 200ml 2M sodium hydroxide. The organic layer was washed with 3x250ml water, dried and concentrated. Fractionation yielded a 3.6g forerun, consisting of 2,2'-dithiophene and 5-bromo-2,2'-dithiophene. The title product was separated by distillation, weight 22.6g (54.3%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.21 (dd, 1H), 7.10 (dd, 1H), 7.01 (dd, 1H), 6.95 (d, 1H), 6.90 (d, 1H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 132.792, 132.214, 130.687, 129.524,.128.691, 127.525, 126.954, 110.128.

(4.23) Synthesis of 3'',4''-dihexyl-2,2'; 5',2''; 5'',2'''; 5''',2''''-pentathiophene

In a 250ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed dry magnesium turnings (1.8g, 0.075moles), a single crystal of iodine and 75ml diethylether. A solution of 5-bromo-2,2'-dithiophene (15.9g, 0.065moles) in 50ml diethylether was placed in the dropping funnel. 10ml of the 5-bromo-2,2'-dithiophene solution was run into the reaction flask. Once the reaction had started (ether boiling and turbid colour) the remainder of the 5-bromo-2,2'-dithiophene solution was added over a twenty minute period, maintaining gentle reflux. Once addition was complete the Grignard was left to stir at room temperature for one hour. In a second 500ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen

bubbler was placed 2,5-dibromo-3,4-dihexylthiophene (12.9g, 0.03moles), [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (0.27g, 0.0005moles) and 50ml diethylether. After cooling, in an ice-bath, the Grignard was added dropwise. Once the addition was complete the resulting adduct was allowed to warm to room temperature and left to stir for forty-eight hours. The resulting dark brown solution was poured carefully onto 200ml 1M hydrochloric acid. The organic layer was washed with 3x100ml water, dried and concentrated. The title product was separated by chromatography on a silica-gel column, eluting with hexane. The title oligomer was thus separated as a red solid, weight 5.69g (32.7%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.30 (m, 8H), 7.07 (m, 2H), 2.77 (t, 4H), 1.71 (p, 4H), 1.33 (m, 12H), 0.97 (t, 6H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 142.870, 133.722, 132.486, 131.009, 130.662, 130.165, 129.861, 127.981, 126.287, 110.278, 32.8102, 30.7619, 30.5210, 30.2107, 23.2877, 14.0129.

(4.24) Synthesis of 2-bromo-3-decylthiophene

Preparation was carried in an identical manner to 2-bromo-3-hexylthiophene, using 3-decylthiophene (20g, 0.09moles) and bromine (14.4g, 0.09moles). The title product was distilled at 125°C / 2mm Hg, weight 10.8g (39.6%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.20 (d, 1H), 6.82 (d, 1H), 2.60 (t, 2H), 1.60 (p, 2H), 1.33 (m, 14H), 0.94 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 142.464, 131.447, 128.736, 125.626, 32.4943, 30.3152, 30.1696, 30.0974, 30.0159, 29.9371, 29.8057, 29.6803, 23.2890, 14.7282.

(4.26) Synthesis of 2,5-dibromothiophene

In a 2L, three necked flask equipped with a stirrer, a dropping funnel and an

outlet for the hydrogen bromide evolved was placed thiophene (84g, 1mole) and 500ml dichloromethane. The flask was then cooled in an ice-bath and bromine (320g, 2moles) was added dropwise to the stirred solution over a period of two hours. The mixture was left to stir overnight and then poured onto 300ml 2M sodium hydroxide. The organic layer was collected and washed with 4x300ml water, dried and concentrated. Fractionation yielded a 7.4g forerun b.pt 78-211°C consisting of thiophene, 2-bromothiophene and 2,5-dibromothiophene. The title product was distilled at 211-212°C, weight 195.3g (80.7%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 6.84 (s, 2H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 130.956, 110.914.

(4.27) Synthesis of 3,3''-didecyl-2,2';5',2''-terthiophene

In a 100ml, three necked flask equipped with a stirrer, a reflux condenser with nitrogen bubbler and a dropping funnel was placed dry magnesium turnings (0.75g, 0.031moles), a single crystal of iodine and 30ml diethylether. 2-bromo-3-decylthiophene (9g, 0.029moles) was added dropwise maintaining a gentle reflux, and left to stir at room temperature for one hour. In a second 250ml, three necked flask equipped with a stirrer, a reflux condenser with nitrogen bubbler and a dropping funnel was placed 2,5-dibromothiophene (2.9g, 0.012moles), [1,3-bis(diphenyl phosphino)propane]-nickel(II) chloride (0.6g, 0.0011moles) and 40ml diethylether. After cooling to 0°C the Grignard was added dropwise. Once addition was complete, the adduct was stirred at room temperature for forty hours. The resulting dark brown solution was poured carefully onto 50ml 1M hydrochloric acid. The organic layer was washed with 2x50ml water, dried and concentrated. The title product was separated as a colourless liquid, by careful chromatography using a silica-gel column and petrol as the elutant, weight 5.24g (82.7%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.20 (m, 4H), 6.95 (d, 2H), 2.65 (t, 4H), 1.56 (p, 4H), 1.31 (m, 28H), 1.05 (t, 6H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 140.546, 127.234, 126.834, 126.143, 125.954,

125.480, 32.4943, 30.3152, 30.1696, 30.0974, 30.0159, 29.9371, 29.8057, 29.6803, 23.2890, 14.7282.

(4.28) Synthesis of 2,5''-dibromo-3,3''-didecyl-2,2';5',2''-terthiophene

Preparation was carried in an identical manner to 2,5-dibromo-3-hexylthiophene, using 3,3''-didecyl-2,2';5',2''-terthiophene (3.8g, 0.0072moles) and bromine (1.15g, 0.0072moles). The title product was thus separated, weight 4.1g (83.0%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.25 (m, 4H), 2.70 (t, 4H), 1.52 (p, 4H), 1.28 (m, 28H), 1.00 (t, 6H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 141.586, 128.934, 127.925, 126.185, 125.854, 111.975, 32.4543, 31.1643, 30.8645, 30.1764, 29.8665, 29.2524, 28.7547, 28.2756, 23.2890, 13.9744.

(4.29) Synthesis of 4',3'''-didecyl-2,2'; 5',2''; 5'',2'''; 5''',2''''-pentathiophene

Preparation was carried out in an identical manner to 3,3''-didecyl-2,2';5',2''-terthiophene, using dry magnesium turnings (0.4g, 0.016moles), 2-bromothiophene (2.1g, 0.013moles), 2,5''-dibromo-3,3''-didecyl-2,2';5',2''-terthiophene (3.2g, 0.0047moles) and 1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (0.27g, 0.0005moles). The title product was thus collected, weight 2.0g (62.4%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.20 (m, 8H), 7.05 (d, 2H), 2.60 (t, 4H), 1.52 (p, 4H), 1.27 (m, 28H), 0.95 (t, 6H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 141.864, 132.746, 131.312, 129.965, 129.276, 128.266, 127.234, 126.143, 126.004, 125.480, 32.4943, 30.3152, 30.1696, 30.0974, 30.0159, 29.9371, 29.8057, 29.6803, 23.2890, 14.7282.

(4.30) Synthesis of 2-bromo-3-hexylthiophene

In a 500ml, three necked flask equipped with a stirrer, a dropping funnel and an outlet for the hydrogen bromide evolved was placed 3-hexylthiophene (16.8g, 0.1moles) and 100ml of acetic acid. The flask was then cooled in an ice-bath and a solution of bromine (16g, 0.1moles) in 50ml acetic acid was added dropwise over a period of forty minutes. The mixture was poured onto 100ml ice-cold water. This was then extracted with 2x100ml dichloromethane. The combined organic layers were washed with 4x100ml water, dried and concentrated. The title compound was distilled at 134°C / 10mm Hg, weight 9.7g (39.3%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.15 (d, 1H), 6.75 (d, 1H), 2.58 (t, 2H), 1.59 (p, 2H), 1.28 (m, 6H), 0.90 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 142.679, 132.018, 128.360, 126.178, 32.5691, 30.4891, 30.2831, 29.7218, 22.8978, 14.8108.

(4.31) Synthesis of 2-bromo-3-octylthiophene

Preparation was carried in an identical manner to 2-bromo-3-hexylthiophene, using 3-octylthiophene (14.6g, 0.074moles) and bromine (11.9g, 0.074moles). The title product was distilled at 159°C / 2.4mm Hg, weight 7.7g (37.8%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.17 (d, 1H), 6.81 (d, 1H), 2.53 (t, 2H), 1.53 (p, 2H), 1.27 (m, 10H), 0.88 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 142.813, 131.984, 128.176, 125.844, 32.7766, 30.5817, 30.3721, 30.1017, 29.9872, 29.6722, 22.9722, 14.7017.

(4.32) Synthesis of poly((3-hexyl)thiophene)

In a 250ml, three necked flask equipped with a stirrer , a dropping funnel and

a rubber septum was placed dry diisopropylamine (5g, 0.05moles) and 75ml THF. At room temperature, n-butyl lithium (20ml, 2.5M in hexane, 0.05moles) was added to the stirred solution. The stirred solution was placed in a liquid nitrogen/acetonitrile bath, reducing the temperature to -42°C. After thirty minutes the temperature was further reduced to -78°C (liquid nitrogen bath) and 2-bromo-3-hexylthiophene (12.4g, 0.05moles) was added. This mixture was then warmed to -42°C and stirred for a further forty minutes. Decreasing the temperature again to -78°C, magnesium bromide etherate (12.9g, 0.05moles) was added and the temperature was allowed to raise to slowly to -5°c over forty minutes. At -5°C, 1,3-bis(diphenylphosphino) propane]-nickel(II) chloride (0.5g, 0.001moles) was added. The resulting mixture was allowed to warm to room temperature overnight. The brown solution was poured onto 200ml methanol. The resulting red precipitate was washed with 2x100ml water, and then dried under vacuum. The dried solid was subjected to Soxhlet extraction. Firstly methanol then hexane, to remove oligomers and impurities followed by dichloromethane to dissolve the polymer. Evaporation followed by drying yielded the title polymer as a red powder 3.6g (43.9%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.12 (s, 1H), 2.78 (t, 2H), 1.73 (p, 2H), 1.31 (m, 6H), 0.89 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 140.045, 133.254, 130.296, 128.946, 32.0273, 30.1844, 29.4274, 29.3755, 22.5324, 13.8965.

(4.33) Synthesis of poly((3-octyl)thiophene)

Preparation was carried out in an identical manner to poly((3-hexyl) thiophene), using dry diisopropylamine (5g, 0.05moles), n-butyl lithium (20ml, 2.5M in hexane, 0.05moles), 2-bromo-3-octylthiophene (13.8g, 0.05moles), magnesium bromide etherate (12.9g, 0.05moles) and 1,3-bis(diphenylphosphino) propane]-nickel(II) chloride (0.5g, 0.001moles). The title product was thus collected by Soxhlet extraction, as a red powder, weight 5.1g (52.6%). ^{1}H-NMR (200MHz)

$\delta(CDCl_3)$ 6.98 (s, 1H), 2.80 (t, 2H), 1.67 (p, 2H), 1.28 (m, 10H), 0.88 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 139.887, 133.694, 130.530, 128.602, 31.9186, 30.5660, 29.7168, 29.5995, 29.4640, 29.3245, 22.7088, 14.1501.

(4.34) Synthesis of poly((3-decyl)thiophene)

Preparation was carried out in an identical manner to poly((3-hexyl) thiophene), using dry diisopropylamine (5g, 0.05moles), butyllithium (20ml, 2.5M in hexane, 0.05moles), 2-bromo-3-decylthiophene (15.2g, 0.05moles), magnesium bromide etherate (12.9g, 0.05moles) and 1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (0.5g, 0.001moles). The title product was thus collected by Soxhlet extraction, as a red solid, weight 5.3g (47.7%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.05 (s, 1H), 2.75 (t, 2H), 1.63 (p, 2H), 1.32 (m, 14H), 0.93 (t, 3H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 140.012, 133.263, 130.163, 129.173, 32.0864, 30.5525, 30.2644, 29.6381, 29.5285, 29.4636, 29.4323, 29.2954, 23.0263, 13.9694.

(4.36) Synthesis of 3-(3-phenylpropyl)thiophene

Preparation was carried in an identical manner to 3-hexylthiophene, using dry magnesium turnings (5.28g, 0.22moles), 1-bromo-3-phenylpropane (30.8g, 0.15moles), 3-bromothiophene (22.8g, 0.14moles) and [1,3-bis(diphenylphosphino) propane]-nickel(II) chloride (1.08g, 0.002moles). The title product was obtained by distillation, weight 17.5g (61.9%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.45 (m, 6H), 7.16 (m, 2H), 2.88 (t, 4H), 2.20 (p, 2H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 143.263, 142.899, 129.223, 129.090, 128.932, 126.544, 125.990, 120.826, 36.1787, 32.8426, 30.5093. MS m/z (relative intensity) 202 (M+ 8), 98 (100), 91 (22), 77

(21), 65 (23).

(4.37) Synthesis of 2-bromo-3-(3-phenylpropyl)thiophene

Preparation was carried in an identical manner to 2-bromo-3-hexylthiophene, using 3-(3-phenylpropyl)thiophene (11.11g, 0.055moles) and bromine (8.8g, 0.055moles). The title product was distilled at 125°C / 0.5mm Hg, weight 6.8g (44.0%). ^{1}H-NMR (200MHz) δ($CDCl_3$) 7.16 (m, 6H), 6.72 (d, 1H), 2.52 (t, 4H), 1.86 (p, 2H). ^{13}C-NMR (50MHz) δ($CDCl_3$) 142.521, 141.880, 131.403, 128.942, 128.869, 128.687, 126.451, 125.869, 35.9361, 31.8619, 29.5919.

(4.38) Synthesis of 2,5-dibromo-3-(3-phenylpropyl)thiophene

Preparation was carried in an identical manner to 2,5-dibromo-3-hexylthiophene, using 3-(3-phenylpropyl)thiophene (10.1g, 0.05moles) and bromine (16.0g, 0.1moles). The title product was thus separated, weight 15.2g (84.4%). ^{1}H-NMR (200MHz) δ($CDCl_3$) 7.25 (m, 5H), 6.90 (s, 1H), 2.72 (t, 4H), 2.00 (p, 2H). ^{13}C-NMR (50MHz) δ($CDCl_3$) 143.008, 142.262, 131.508, 129.102, 129.029, 126.576, 111.202, 108.943, 35.9563, 31.7669, 29.7672.

(4.39) Synthesis of 3'-(3-phenylpropyl)-2,2';5',2''-terthiophene

Preparation was carried in an identical manner to 3'-hexyl-2,2';5',2''-terthiophene, using dry magnesium turnings (0.79g, 0.033moles), 2-bromothiophene (5.13g, 0.031moles), 2,5-dibromo-3-(3-phenylpropyl)thiophene (5.4g, 0.015moles) and [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (0.3g, 0.0006moles).

The title product was thus separated, weight 3.58g (65.2%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.21 (m, 10H), 7.02 (m, 2H), 2.63 (m, 4H), 1.87 (m, 2H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 143.045, 142.266, 138.045, 131.532, 129.041, 128.428, 127.915, 127.488, 127.415, 126.904, 126.366, 124.961, 124.757, 124.374, 111.218, 108.943, 35.9562, 31.7612, 29.7532.

(4.47) Synthesis of 3-phenylthiophene

Preparation was carried in an identical manner to 3-hexylthiophene, using dry magnesium turnings (2.64g, 0.11moles), phenylbromide (16.5g, 0.105moles), 3-bromothiophene (16.3g, 0.1moles) and [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (1.08g, 0.002moles). The title product was thus separated by chromatography on a silica column using hexane, as a colourless liquid, weight 10.2g (63.8%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.30 (m, 6H), 7.05 (m, 2H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 142.384, 136.023, 128.637, 127.283, 126.394, 126.143, 126.003, 120.235.

(4.48) Synthesis of 2,5-dibromo-3-phenylthiophene

Preparation was carried in an identical manner to 2,5-dibromo-3-hexylthiophene, using 3-phenylthiophene (7g, 0.044moles) and bromine (14g, 0.088moles). The title product was thus separated by chromatography, as a colourless liquid, weight 11.5g (82.2%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.25 (m, 6H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 132.844, 129.365, 129.088, 127.848, 127.719, 114.271, 112.799, 111.345

(4.51) Synthesis of 1,4-Di-(2-(3-hexyl)thienyl)benzene

In a 250ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed dry magnesium turnings (1.5g, 0.063moles), a single crystal of iodine and 20ml diethylether. A solution of 2-bromo-3-hexylthiophene (14.8g, 0.06moles) in 50ml diethylether was placed in the dropping funnel. 10ml of the 2-bromo-3-hexylthiophene solution was run into the reaction flask. Once the reaction had started (ether boiling and turbid colour), a further 50ml of diethylether was added to the reaction flask. The remainder of the 2-bromo-3-hexylthiophene solution was added over a ten minute period, maintaining gentle reflux. Once addition was complete the Grignard solution was left to stir at room temperature for one hour. In a second 500ml, three necked flask equipped with a stirrer, a dropping funnel and a reflux condenser with nitrogen bubbler was placed 1,4-dibromobenzene (6.4g, 0.025moles), [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (0.16g, 0.0003moles) and 50ml diethylether. After cooling, in an ice-bath, the Grignard solution was added dropwise. Once the addition was complete the resulting adduct was allowed to warm to room temperature and left to stir for twenty hours. The resulting dark brown solution was poured carefully onto 100ml 1M hydrochloric acid solution. The organic layer was washed with 3x100ml water, dried and concentrated. The crude product was purified on a silica-gel column eluting with hexane. The title product was thus separated, as a colourless liquid, weight 6.47g (63.2%). ^{1}H-NMR (200MHz) $\delta(CDCl_3)$ 7.35 (s, 4H), 7.25 (d, 2H), 7.05 (d, 2H), 2.75 (t, 4H), 1.69 (p, 4H), 1.34 (m, 12H), 0.92 (t, 6H). ^{13}C-NMR (50MHz) $\delta(CDCl_3)$ 141.432, 135.687, 130.632, 127.954, 125.876, 121.532, 32.8266, 30.7487, 29.4654, 28.3766, 22.2765, 14.2870.

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4.11 List of Chemicals and Products

4.1 Thiophene.

4.2 2,3,5-Tribromothiophene.

4.3 3-Bromothiophene.

4.4 3-Hexylthiophene.

4.5 3-Octylthiophene.

4.6 3-Decylthiophene.

4.7 3-Hexadecylthiophene.

4.8 2,5-Dibromo-3-hexylthiophene.

4.9 2,5-Dibromo-3-decylthiophene.

4.10 2-Thienyl magnesium bromide.

4.11 3'-Hexyl-2,2';5',2''-terthiophene.

4.12 3'-Decyl-2,2';5',2''-terthiophene.

4.13 β',β''''-Dihexyl-2,2';5',2'';5'',2''';5''',2'''';5'''',2'''''-sexithiophene.

4.14 β',β''''-Didecyl-2,2';5',2'';5'',2''';5''',2'''';5'''',2'''''-sexithiophene.

4.15 1,2,3,4-Tetrabromothiophene.

4.16 3,4-Dibromothiophene.

4.17 3,4-Dihexylthiophene.

4.18 2,5-Dibromo-3,4-dihexylthiophene.

4.19 2-Bromothiophene.

4.20 2,2'-Dithiophene.

4.21 5-Bromo-2,2'-dithiophene.

4.22 5-(2-(2'-thienyl)thienyl) magnesium bromide.

4.23 3'',4''-Dihexyl-2,2';5',2'';5'',2''';5''',2''''-pentathiophene.

4.24 2-Bromo-3-decylthiophene.

4.25 (2-(3-Decyl)thienyl) magnesium bromide.

4.26 2,5-Dibromothiophene.

4.27 3,3"-Didecyl-2,2';5'.2"-terthiophene.

4.28 5,5'"-Dibromo-3,3"-didecyl-2,2';5'.2"-terthiophene.

4.29 4',3'"-Didecyl-2,2';5',2";5",2'";5'",2"";5"",2""-pentathiophene.

4.30 2-Bromo-3-hexylthiophene.

4.31 2-Bromo-3-octylthiophene.

4.32 Poly((3-hexyl)thiophene).

4.33 Poly((3-octyl)thiophene).

4.34 Poly((3-decyl)thiophene).

4.35 3-(3-Phenylpropyl) magnesium bromide.

4.36 3-(3-Phenylpropyl)thiophene.

4.37 2-Bromo-3-(3-phenylpropyl)thiophene.

4.38 2,5-Dibromo-3-(3-phenylpropyl)thiophene.

4.39 3'-(3-Phenylpropyl)-2,2';5',2"-terthiophene.

4.40 3-(ω-Bromoalkyl)thiophene.

4.41 ω-(*p*-Methoxyphenoxy)alkyl bromide.

4.42 α,ω-Dihaloalkane.

4.43 Hydroquinone monoethyl ether.

4.44 3-[ω-(*p*-Methoxyphenoxy)alkyl] thiophene.

4.45 [ω-(*p*-Methoxyphenoxy)alkyl] magnesium bromide.

4.46 Phenyl magnesium bromide.

4.47 3-Phenylthiophene.

4.48 2,5-Dibromo-3-phenylthiophene.

4.49 (2-(3-Hexyl)thienyl) magnesium bromide.

4.50 1,4-Dibomobenzene.

4.51 1,4-Di-(2-(3-hexyl)thienyl)benzene.

Chapter Five

Electrochemistry of Polythiophenes

5.1 Introduction

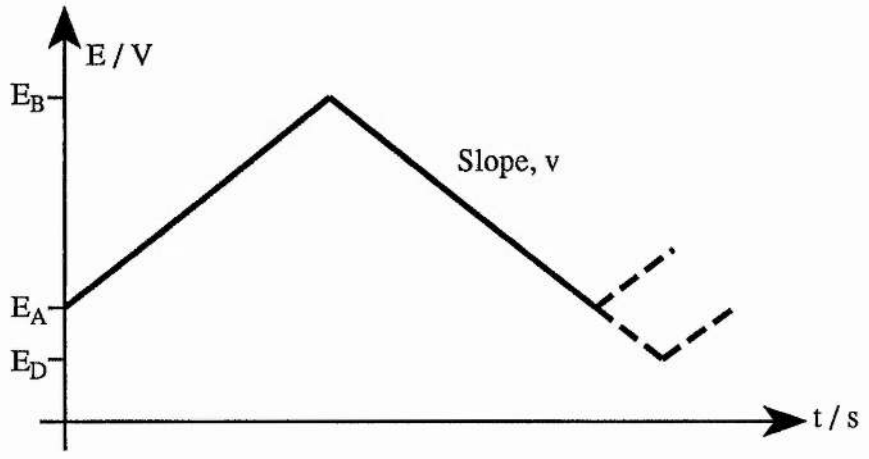
For 170 years following the pioneering electrochemical work of men such as Faraday and Volta, electrochemists were content with the study of electron transfer at the metal-solution interface. Over the last thirty years this has rapidly changed as the possibilities offered by the electrochemistry of semiconducting materials and the phenomenon of the 'modified electrode' have been explored. As a result of these advances, various types of coated electrodes are now common place in the laboratory. These advances have led to the development of new fields of chemistry, such as photoelectrochemistry. Significant technological advances have also been made, and many changes have been made to traditional electrochemical devices, e.g. capacitors.

This Chapter details investigations into the electrochemical synthesis of polythiophene. To simplify this discussion, the Chapter has been split into four sections. Firstly the principles of electrochemistry are discussed, including an insight into some of the theory and applications. In particular, the usefulness of cyclic voltammetry (CV) as a diagnostic tool is explored in greater detail. This is closely followed by a description of our particular cell, electrodes and the instrumentation set-up. Next, a literature review of significant work reported hitherto on the electrochemistry of polythiophenes. The remaining section deals with the electrochemistry of the four oligothiophenes and the three polythiophenes prepared, as described in the preceding Chapter.

5.2 Principles of Electrochemistry

The principles of electrochemistry have been described in many famous textbooks[5.1, 5.2]. In addition, the application of electrochemistry to the study of polythiophene has been fully detailed in literature[5.3] and is explored in greater detail in Section 5.4. Cyclic voltammetry has emerged as the most popular technique, largely as a diagnostic tool for the initial characterisation of a redox polymer (or indeed any electrochemical system). In this initial characterisation information can be gained about the kinetics of a system, the oxidation and reduction potentials of the system and the species which might be present. The polymer under investigation can either be preformed and deposited onto the electrode surface, using techniques such as spin coating, or formed on the electrode during the potential cycling process.

The potential-time waveform used in sweep measurements is depicted in Figure 5.1. Before the advent of modern electronics, the simplest experiment, linear sweep voltammetry, involved the electrode potential being swept between E_A and E_B at a known sweep rate, v, before stopping the potential sweep. Nowadays, a more



Potential-time profiles for sweep voltammetry.

Figure 5.1

useful technique, however, is cyclic voltammetry. Cyclic voltammetry again involves sweeping the potential of an electrode (the working electrode (WE)) within fixed limits and at a constant scan rate. Here the waveform is initially the same, but when the potential reaches E_B the sweep is reversed. When the potential again reaches E_A several things can happen. The sweep can be terminated, reversed again, or continued to another potential value E_D. In all these cases measurements of current relative to the WE and a reference electrode (RE) are made. A graph is then plotted of the current as a function of the potential. These graphs, called voltammograms, have some basic components which are detailed in Figure 5.4.

In a typical study of thiophene polymerisation, voltammograms are recorded over a wide range of scan rates and for various values of E_A, E_B and E_D. Generally, the sweep begins at a potential at which no faradaic processes occur (e.g. 0V), increases to a positive value, then sweeps back through 0V to a negative value before returning to the origin, hence completing the first sweep. There will be several peaks in the voltammogram. From the behaviour of these peaks as the potential limits and scan rates are changed, and also from the difference between the first and subsequent scans, we can learn about the nature of the processes occurring. Also from the dependence of the peak height on scan rate the role of adsorption, diffusion and coupled homogenous chemical reactions can be identified. This technique was first reported by Sevcik[5.4] in 1948. This publication was closely followed by others which outlined the theory of the technique. The most famous of these are the works by Nicholson and Shain[5.5, 5.6] which laid the ground rules for future work, such as work by Saveant *et. al.*[5.7, 5.8], expanding the theory to convolution cyclic voltammetry, which uses a sophisticated mathematical treatment of the data.

Scan rates can vary from a few mVs^{-1} to a few hundred Vs^{-1}. The higher currents reached at high scan rate can lead to complications. Double layer charging causes large background currents, $i_{dl} = vC_{dl}$ where C_{dl} is the double layer capacity.

The higher currents produced at higher scan rates causes greater iR_u voltage drops tending to distortion of the response (R_u = uncompensated resistance). The use of cyclic voltammetry has now become more commonplace as the instrumentation has improved and became more affordable. Scan rates as high as $10{,}000Vs^{-1}$ can be easily utilised by using micro electrode technology and computing power to analysis and manipulate the data.

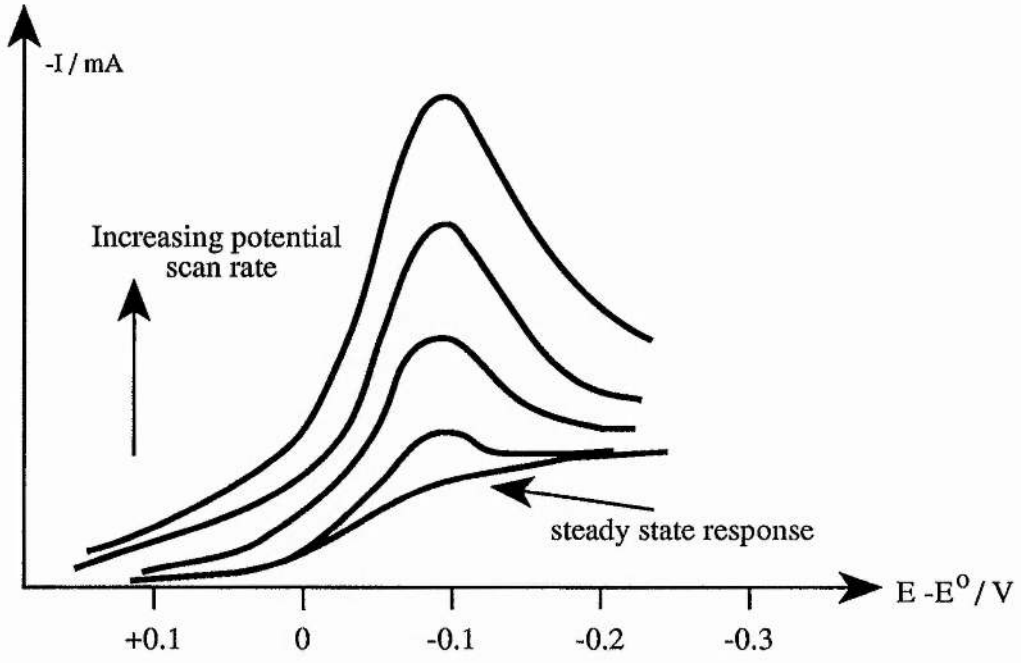
The theory behind cyclic voltammetry is a very complex one based on the solution of differential equations and has been fully discussed else where[5.9, 5.10]. A brief review of the important aspects shall be outlined below. Consider the simple reversible reaction, Eq. 5.1, where initially only O is present, in a rapidly stirred electrochemical cell.

$$O + ne^- \rightleftharpoons R \qquad \text{Eq: 5.1}$$

If the sweep rate, v, is slow then the recorded voltammogram will compare to the steady state I vs E curve. Upon increasing the scan rate a peak of increasing height appears - Figure 5.2. This is due to the concentration profile as a function of the potential. Under steady-state conditions the concentrations at a certain distance from the electrode surface are maintained uniform due to stirring and natural convection. The region next to the electrode, the Nernst diffusion layer, has linear concentration gradients. The ratio of surface concentrations $c_O{}^\sigma / c_R{}^\sigma$, for a reversible reaction, is given by the Nernst equation, Eq: 5.2.

$$E = E^o + \frac{RT}{nF} \ln \frac{c_o{}^\sigma}{c_R{}^\sigma} \qquad \text{Eq: 5.2}$$

As the potential goes more negative the surface concentration of the reactants must decrease. Thus the current must increase to compensate for the increase in the



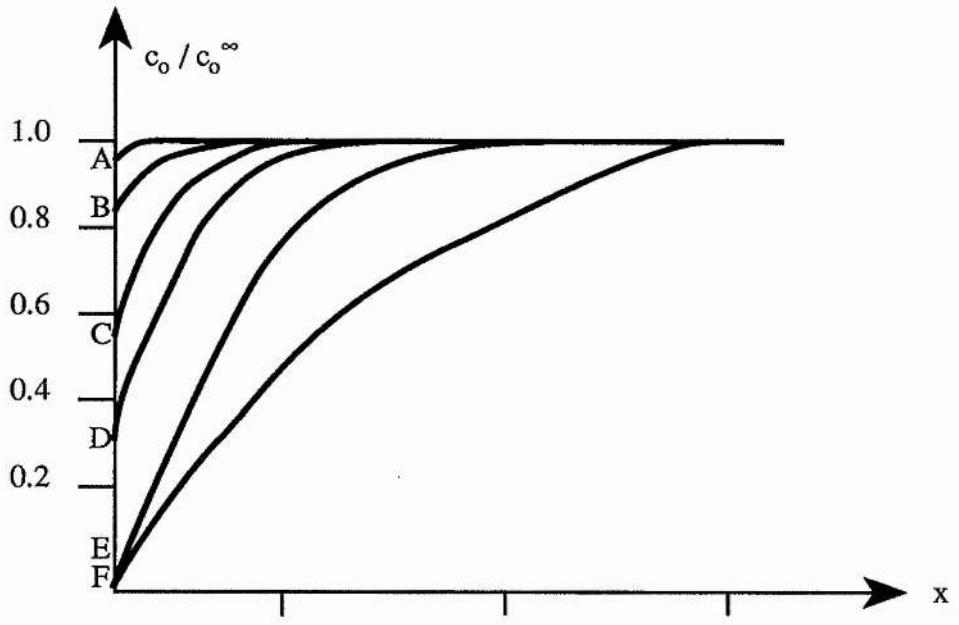
Linear sweep voltammograms for the reaction

$O + e^- \longrightarrow R$, at several potential scan rates.

Figure 5.2

concentration gradient. This continues until the surface concentration approaches zero and so the steady state concentration profile cannot change further and the current reaches a plateau. If the increase in scan rate is continued there will reach a point where there is insufficient time for the diffusion layer to return to the equilibrium state. The Nernst diffusion layer does not extend far into the solution. A series of concentration profiles are outlined in Figure 5.3.

As soon as the potential is reached where O is reduced, the surface concentration of O decreases from the bulk value, hence obeying the Nernst equation (Eq: 5.2), and so a concentration gradient is set up - Figure 5.3(A). As a result, a current which is proportional to the value of the gradient at the electrode, flows in the



Concentration-distance profiles for the electroactive species, O, in the reaction $O + e^- \longrightarrow R$ during a linear potential sweep experiment. The curves correspond to the potentials: (A) E^o +90mV; (B) E^o +50mV; (C) E^o 0mV; (D) E^o -28mV; (E) E^o -128mV; and (F) E^o -280mV.

Figure 5.3

external circuit. Once the gradient is set up, diffusion causes a decrease in concentration. The electrode potential is still changing and so the surface concentration of O is further decreased (B) and (C) until it reaches zero (D). At any given potential the concentration is greater than the steady-state and so the current is larger. Once $(c_O)_{x=0}$ reaches zero the concentration gradient starts to decrease, due to the relaxation effect (E) and (F) and hence the current flowing must also decrease. The overall effect is the peak current-potential curves as shown in Figure 5.2.

In an electrochemical system there are two main rate determining steps for the process. The first of these is the rate of transfer of the electron. This has been fully

described by Nicholson[5.11]. The second rate determining step is the rate of mass transport. This can split into three sections to enable discussion of each in detail: (a) convection; (b) diffusion; and (c) migration. One must remember, however, that all three are occurring concurrently.

(a) Convection:- Stirring or hydrodynamic transport characterises this form of mass transport. Generally fluid flow occurs because of natural convection (convection caused by density gradient) and forced convection, and may be characterised by stagnant regions, laminar flow and turbulent flow. If an experiment is run for a prolonged period then natural convection will occur. This causes random effects within the cell as noticed by unusual peaks in the cyclic voltammograms. This problem can be simply overcome by stirring the solution or rotating the electrode to obtain a fixed convection rate.

(b) Diffusion:- This form of mass transport concerns the movement of species under the gradient of chemical potential, thus a concentration gradient is set-up. This can lead to a depletion of the electroactive species at the electrode. If steady-state currents are required (e.g. during an electrolysis) then an external force must be applied to maintain the concentration profile at the electrode surface. Simple stirring improves this fundamental problem, and many more sophisticated techniques practically eliminate the effect: rotating disk electrode; rotating ring electrode; dropping mercury electrode; microelectrodes; and many forced flow solution systems.

(c) Migration:- This form of mass transport concerns the movement of a charged body under the influence of an electric field, hence a gradient of electric potential is achieved. Migration of ions carries the current in the bulk solution during electrolysis. As will be outlined below, this form of mass transport has little or no effect at the electrode surface, and can hence be ignored.

As mentioned above, convection will only affect the cyclic voltammogram of a system if the time scale of an experiment is prolonged. Therefore in the context of our systems, which are rapidly carried out, we shall assume that only diffusion affects the rate determining step of our cyclic voltammograms.

The faradaic current (i_f) can thus be expressed as the sum of two components, the migrational component (i_m) and the diffusional component (i_d) of the electroactive species at the electrode, assuming fast electron transfer leading to Nernstian behaviour.

$$i_f = i_m + i_d \qquad \text{Eq: 5.3}$$

This equation can be further simplified by suppressing the migrational flux of the components. This is readily achieved by the addition of sufficient concentration of a non-electroactive species, the supporting electrolyte. Thus most of the observed current can be attributed to i_d as the migration component of the electroactive species will be small compared to that of the supporting electrolyte. This, in fact, is the case for most electrochemical systems where the theories have been worked out to deal with purely diffusional currents. Therefore the addition of a supporting electrolyte, generally 50-100 fold excess, has the effect of suppressing i_m and simplifying the system.

Assuming that in an electrochemical system the kinetics of the various components are sufficiently fast, then the system will follow the Nernst equation (Eq: 5.2) and the system is called a reversible one. For any reversible system the cyclic voltammogram will have various components that are similar. Figure 5.4 outlines the basic cyclic voltammogram of a reversible process where E_p^a and E_p^c are the potential values for the peak anodic and cathodic currents and I_p^a and I_p^c represent the respective current densities.

For the reversible system, solving Flick's second law for O and R, Eq: 5.4 and Eq: 5.5 respectively,

$$\frac{\delta C_O}{\delta t} = D_O \frac{\delta^2 C_O}{\delta x^2} \qquad \text{Eq: 5.4}$$

$$\frac{\delta C_R}{\delta t} = D_R \frac{\delta^2 C_R}{\delta x^2} \qquad \text{Eq: 5.5}$$

with the appropriate conditions and allowing $D_O = D_r + D$, leads to:

$$I_p = -0.446\, nF \left(\frac{nF}{RT}\right)^{1/2} c_o D^{1/2} v^{1/2} \qquad \text{Eq: 5.6}$$

where: I_p = peak current density (Acm^{-2}); D = diffusion co-efficient (cm^2s^{-1}); v = scan rate (Vs^{-1}); and c_O = bulk concentration (mol cm^{-3}). This equation is known as the Randles-Sevcik equation.

Certain diagnostic tests exist for the cyclic voltammograms of the reversible process.

1	$E_p = E_p^a - E_p^c = 59/n$ (mV).	2	$E_p - E_{p/2} = 59/n$ (mV).
3	$I_p \alpha v^{1/2}$.	4	$I_p^a / I_p^c = 1$.
5	at potentials beyond E_p, $I^{-2} \alpha t$.	6	t_p is independent of v.

The above are true in a reversible system but in an irreversible (in the sense of electrode kinetics) situation these conditions do not apply. An irreversible system occurs when the rate of electron transfer is insufficient to maintain the Nernstian equilibrium at the electrode surface. The most noticeable difference in the cyclic voltammogram of an irreversible system is that there is no reverse peak. One has to apply extra conditions to ensure that the system is in fact irreversible. The lack of a reverse peak is not conclusive, as this may be due to the presence of a follow up

chemical reaction after the initial oxidation (or reduction) of the species. Also, as was discussed in Chapter 3, the formation of a polymer on the electrode may lead to electrode passivation due to the formation of an insulating polymer on the electrode surface.

Similar to the reversible system there are certain criteria which can be studied to check that the system is in fact irreversible.

1 No reverse peak.

2 $E_p - E_{p/2} = 48/\alpha_a n_a$ (mV).

3 E_p^a shifts $30/\alpha_a n_a$ (mV) for each decade increase in v.

4 $I_p^a \propto v^{1/2}$.

In addition to these there are various criteria depending upon which system one is studying, e.g. for EC systems. Also it is noticeable that some of these criteria apply only to certain distinct kinetic regions. One therefore has to be careful in applying general criteria and expecting the system to obey the criteria to the letter. For a fuller understanding of this topic see the work of Saveant *et. al.*[5.12].

As an example, in an EC reaction (Electrochemical step followed by a Chemical reaction) the general criteria are.

1 I_p^c / I_p^c is less than 1, but tends to unity as v is increased.

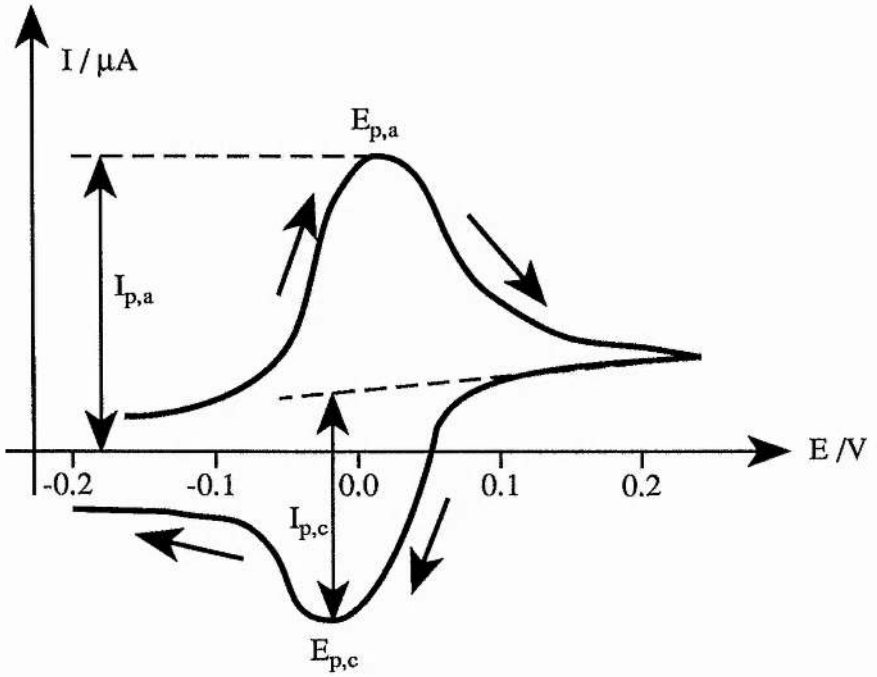
2 $I_p^a / v^{1/2}$ decreases slightly with increasing v.

3 E_p^a is negative of the value for the reversible case.

4 E_p^a shifts positively with increasing v, and for a first order reaction it will shift by 30/n (mV) per decade increase in v.

It must be noted that the dependence of E_p^a on v will alter upon the kinetics of the EC

system. The above example is just a taste of what can be done with cyclic voltammetry and it is easy to picture the qualitative information that can be obtained from the study of the electrochemistry of a system.



Basic cyclic voltammogram for a reversible process.

Figure 5.4

While the above theory is true for solution electrochemistry, there are some special criteria which must be considered when working with films. For a more detailed review see Murray[5.13]. In short, when the film is sufficiently thick and/or scan rate is sufficiently fast the film behaves as if it is a layer of solution in contact with the electrode and a CV resembling the solution CV shown in Figure 5.4 is observed. This is because a fraction of the film is electrolysed during a scan and the finite nature of the film has no influence. However, if the film is thick and/or the scan rate is slow such that $\partial = \sqrt{2Dt} < l$ where D is the diffusion coefficient, t is the characteristic time and l is the thickness of film. Then the entire film is electrolysed

during the scan. This means that the area under the anodic peak corresponds to the amount of charge needed to electrolyse the film. This charge must remain constant whatever the scan rate, so one will observe a linear increase in peak height with scan rate. The relation is given by:

$$I_p = \frac{n^2F^2A\Gamma_T\nu}{4RT} \qquad \text{Eq: 5.7}$$

where Γ_T is the coverage in mol cm^{-2}. The peak shape is symmetrical because beyond the redox potential (peak maximum) the amount of reduced material becomes depleted as the film boundary is reached and the anodic current decreases, eventually to zero as the film is fully oxidised. Such behaviour is observed for ideal systems such as monolayers and some redox polymers. However conducting polymers show a much more complex response since the redox events are accompanied by large structural and conformational changes within the polymer. The effect of this is noted by a deviation from the expected ideal current / voltage response.

5.3 Experimental

There are many documented systems for the determination of electrochemical data[5.14, 5.15]. In all experimental analysis it is essential that we have precise control and/or measurements of the potential and current flowing. No matter what system is being used there are many features in common. All electrochemical cells consist of electrodes and electrolytes together in some form of container. The diversity of these cells is too in-depth to be included in this discussion. Therefore this section only gives a brief review of the particular aspects of experimental electrochemistry appropriate to my work. To again simplify this discussion the three main topics: electrodes; instrumentation; and cell set-up have been sub-sectioned to enable clarification of

certain aspects as important of our electrochemical work.

5.3.1 Electrodes

Typical with the majority of electrochemical work, our system employs three electrodes: (a) the working electrode, which defines the interface under study; (b) a reference electrode, which maintains a constant reference potential; and (c) a counter (sometimes called secondary) electrode, which supplies the current. A more detailed investigation of the three electrodes is outlined below.

(a) Working electrode:- The design of the working electrode simply depends on the system under analysis. The electrode must essentially be chemically inert to the electrolytic solution, the most common being lead, vitreous carbon, gold and platinum. Taking this into account the electrode can be: a metal foil; a single crystal of a semiconducting film or a metal; an evaporated film and; a powder as a pressed pellet or disc. Theoretically electrodes can be large or small, but commonly, due to various experimental reasons, they are relatively small (<0.25 cm^2). The electrode surface should be perfectly smooth as this will lead to better mass transport. To obtain this perfect smoothness and maintain consistency the solid electrodes are subjected to vigorous pretreatment to ensure a reproducible state of oxidation, surface morphology and freedom from adsorbed impurities. This was achieved, in our case by washing the electrode in acetone followed by polishing the surface with alumina of fixed sizes down to 0.05μm. Finally the electrode tip was placed in an ultrasonic bath to remove any adsorbed particles of alumina. For our exploratory studies, a simple platinum bead electrode was prepared by sealing 0.5mm diameter platinum wire in Pyrex and polished flat. The area of the electrode was $2x10^{-3}m^2$. In order to prepare large area films a platinum foil (area $1cm^3$) was used.

(b) Reference electrode:- The role of this electrode is to provide a fixed potential which does not vary during the experimental analysis (i.e. it should be independent of the current density). It is normal practice to reduce the potential of the reference electrode to other scales, the standard for theoretical studies, being the normal hydrogen electrode. The reference electrode serves a dual purpose by providing a thermodynamic reference and also isolates the working electrode as the system under study. However, the reference electrode must draw some current to enable the measurement to take place, therefore a good reference electrode should be able to maintain a constant potential even if a few microamps are passed through its surface. In our simple system the reference electrode was a commercial saturated calomel electrode (SCE) or a Ag/Ag^+ electrode. The later was prepared by dipping a 0.5mm silver wire into a fritted tube containing the electrolyte solution (e.g. acetonitrile and 0.1M TBAT) with the addition of 10mM $AgBF_4$.

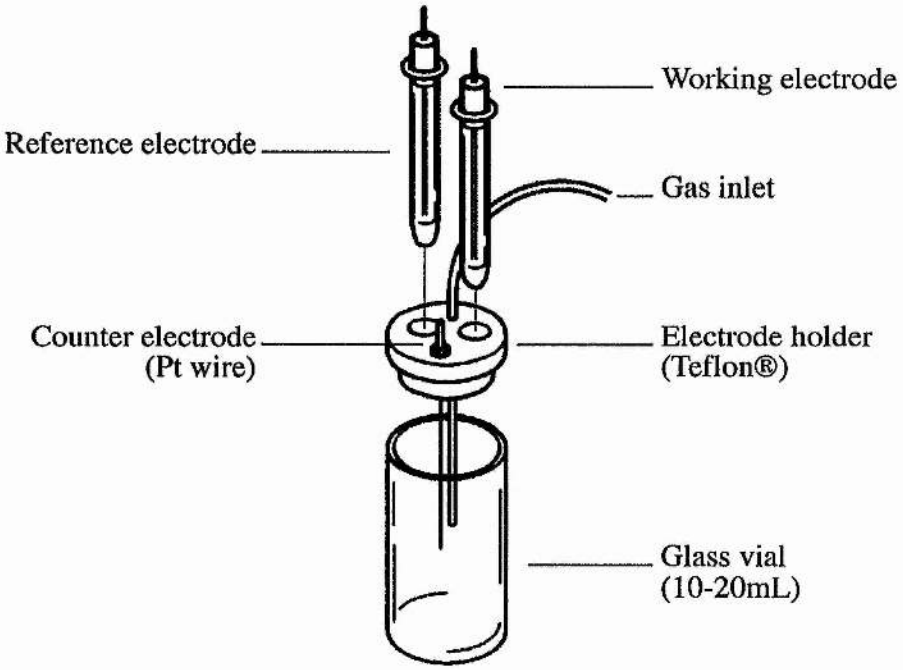
(c) Counter electrode:- The counter electrode must supply the current required by the working electrode without in any way limiting the measured response of the cell. This is particularly important during electrolysis or the preparation of large area conducting films and is achieved by ensuring that the electrode process is a decomposition or a reduction/oxidation of the electrolyte medium, so that a large overpotential is not required and the current flows freely. During such electrolysis the products obtained from the counter electrode must always be considered, since they must not interfere with the reaction under investigation. This can be difficult in certain systems and there are many documented solutions. The major solution to this problem is the separation of the anolytic and catholytic solutions. This can easily be achieved using a frit or an ion exchange membrane. For our diagnostic cyclic voltammetry of conducting polymer electrosynthesis, none of these problems were encountered and a simple platinum wire (99.99%, Aldrich) was used as the counter electrode.

5.3.2 Instrumentation

The cyclic voltammograms were recorded using one of many systems. This in itself shows how fast the field of electrochemistry is growing, three different set-ups during the course of this thesis! The initial cyclic voltammograms where recorded using a Pine Instruments RDE4 potentiostat connected to a Graphtec WX3200 X-Y recorder. The instrumentation was set up to manually plot our cyclic voltammograms in the standard format. This is with the potential being plotted on the y-axis and the current being plotted on the x-axis. The origin was the zero point for both the potential and the current. The two newer methods involved computer controlled inputs and outputs, either an E. G. & PARC 273A interfaced with a PC, or an EcoChimie μAutolab with PC control. Although the later of these systems produced clearer cyclic voltammograms and performed all electrochemical calculations, the cyclic voltammograms printed within this thesis have been scanned and manipulated using 'Abode's Phototshop™ 2.5.1 LE' operating on a Macintosh Performa 6200, to enable all systems to be displayed in the same format and with the comparable resolution.

5.3.3 Cell Set-Up

Our electrochemical analysis were carried out in a simple glass voltammetry cell containing a Teflon® top which holds the three electrodes and the nitrogen inlet tube. Figure 5.5 outlines this simple cell which was held, over a magnetic stirrer, by a clamp. Before beginning with the experimental studies the cell was set-up without the electroactive species under study. After scrupulously cleaning the cell and electrodes, 10-20mL of the solvent and the supporting electrolyte where placed in the cell. The magnetic stirrer was started, and continued throughout the experiment to maintain a fixed convection rate. The solution was degassed, by bubbling nitrogen through the solution for a few minutes. Degassing serves to eliminate any dissolved oxygen from



Basic electrochemical cell set-up.

Figure 5.5

the solution. Oxygen has to be removed as it is always reduced, in protonic solutions through the peroxide to the hydroxide ion, similarly, in aprotic solutions to the superoxide and peroxide ion.

The choice of solvent and supporting electrolyte is essentially determined by the species under investigation and the type of electrodes being used. Certain electrode systems need specific solvents and electrolytes, but for our system which used the simplest of electrodes, we only had to make sure that the species under investigation was soluble in the solvent of choice. For our mixed heterocycles the solvent of choice was acetonitrile. Our choice for the electrolytic salt was tetrabutylammonium tetrafluoroborate (TBAT). As mentioned previously the supporting electrolyte plays an

important role in the electrochemical investigation. The primary role, of the supporting electrolyte, is to effectively eliminate migration as a form of mass transport for the electroactive species. As the supporting electrolyte is in great excess and the transport of ions is proportional to the concentration of ions present, the majority of the charge in the solution will be carried by the supporting electrolyte. The supporting electrolyte also helps to increase the conductivity of the solution and hence reduce the resistance between the working and counter electrode.

5.4 Literature Review

Polythiophene, as might be expected, exhibits many properties similar to those of polypyrrole[5.16]. The electrochemistry of polypyrrole has been extensively discussed by Chandler and Pletcher[5.17]. For an excellent review of the recent advances in the electrochemistry of many conducting polymers, including polypyrrole and polythiophene see the monograph of Evans[5.18]. The chemical synthesis of polythiophene yields an infusible black powder which is insoluble in common solvents[5.18] and is thermally stable in air at temperatures up to 360°C. The conductivity of these chemically prepared polythiophene ranges from $10^{-11}\Omega^{-1}cm^{-1}$ in the neutral form[5.20] to $10^{2}\Omega^{-1}cm^{-1}$ when doped[5.21].

In contrast, the electrochemical synthesis of polythiophene, which was first reported in 1980[5.22], using methods similar to those developed for polypyrrole[5.23], gives a product with conductivity ranging from 10^{-3} to $10^{-1}\Omega cm^{-1}$. This initial work was quickly expanded as other workers[5.24, 5.25] repeated the technique using a number of supporting electrolytes and various solvents. Polymerisation of thiophene onto Pt-coated glass produced thin films from acetonitrile solutions containing small amounts of water[5.26], and also from THF[5.27]. Kaneto *et. al.*[5.28], produced similar results using monomer solutions in oxygen-free anhydrous solvents (acetonitrile or

benzonitrile) and ITO glass substrates. This confirms the similarity between polythiophene and polypyrrole. Diaz[5.29] reported, for pyrrole, that no polymerisation occurs in the absence of oxygen and water unless a suitable counter electrode couple is provided. This can be achieved by using a supporting electrolyte e.g. $AgClO_4$, similar to thiophene.

There have been many substituted thiophenes electrochemically polymerised[5.30, 5.31, 5.32, 5.33, 5.34] . Along with a series of polycyclic monomers that contain a thiophene ring[5.35, 5.37], and dithieno-thiophene monomers[5.36], there has also been a series of compounds consisting of two thiophene rings linked by a polyene chain[5.37]. Table 5.1 details some of the reported monomers and the cell set-up and the reported conductivities. The simple polythiophene has been prepared not only from thiophene monomer[5.38, 5.39, 5.40, 5.41], but from the thiophene dimer[5.42, 5.34], and tetramers[5.40]. In fact many reports have shown that the thiophene dimer gives rise to a higher quality of polythiophene film than is obtained from the monomer[5.35, 5.40]. Table 5.2 lists some of the reported conditions, monomers and electrolytes for the preparation of polythiophene.

The general mechanism for the electrochemical polymerisation of polythiophenes, similar to that of many other monomers[5.43, 5.44], is via a radical coupling mechanism[5.45]. This radical coupling yields mainly α-α linkages[5.46, 5.47], and involves oligomer as well as monomer radicals, with evidence that the polymerisation reaction occurs at a lower potential on existing polymer than on bare metal[5.44]. Chapter One - Scheme I.IV outlines the electropolymerisation technique.

Polythiophene films can be electrochemically cycled from the neutral to the conducting state, high coulombic efficiencies in excess of 95% have been reported[5.48]. There is little evidence of decomposition of the polymers up to +1.4V vs. SCE in acetonitrile[5.49], the 3-methyl derivative being particularly stable[5.50].

Ref	Monomer(conc)	Electrolyte(conc)	Counter Ion	Electrode / Solvent	E_{pot}(V)[a]	$\sigma(\Omega^{-1}cm^{-1})$
5.30	3-bromothiophene	Et_4NBF_4 (0.5M)	---	Pt / acn	+2.10 (CV)	---
5.31	3-methylthiophene (0.2M)	Bu_4NClO_4 (0.02M)	ClO_4^-	ITO / nbz / 5°C / Ar	2mA cm^{-1}	120
5.32	3-ethylthiophene (0.2M)	Et_4NBF_4 (0.03M)	BF_4^-	ITO, Pt / pc / 5°C / Ar	5-10mA cm^{-1}	270
5.33	3-hexylthiophene (0.2M)	Et_4NPF_6 (25mM)	PF_6^-	ITO / pc / 5°C / Ar	2mA cm^{-1}	95
5.33	3-octylthiophene (0.2M)	Et_4NPF_6 (25mM)	PF_6^-	ITO / pc / 5°C / Ar	2mA cm^{-1}	78
5.33	3-icosylthiophene (0.2M)	Et_4NPF_6 (25mM)	PF_6^-	ITO / nbz / 5°C / Ar	2mA cm^{-1}	11
5.34	2,3-dimethylthiophene	Et_4NBF_4 (0.5M)	BF_4^-	Pt / acn	+1.35	50 (pellet)
5.35	dithienobenzene	Et_4NBF_4 (0.5M)	BF_4^-	acn	+1.3	4.4×10^{-4}
5.36	thieno-3,2b-thiophene	Bu_4NClO_4 (0.1M)	BF_4^-	Pt / CH_2Cl_2(anhyd) / Ar	+1.4	3×10^{-4}
5.37	2,5-di(thienyl)pyrrole	AgOTs (85mM)	OTs	Au / acn / N_2	-0.5 to -0.2	10^{-8}
5.37	dithenylethylene	Bu_4NClO_4 (0.05M)	HSO_4^-	Pt / acn / Ar	2mA cm^{-1}	3.7×10^{-6}

Electrochemical synthesis of substituted polythiophenes.

a Potentials measured vs. SCE, if current density only quoted in original ref. this is in place of potential.

Table 5.1

Ref	Monomer(conc)	Electrolyte(conc)	Counter Ion	Electrode / Solvent	E_{pot}(V)[a]	$\sigma(\Omega^{-1}cm^{-1})$
5.38	thiophene (0.01M)	Bu_4NBF_4	BF_4^-	Pt / acn	+1.6	10-100
5.39	thiophene (0.06M)	$LiBF_4$ (0.1M)	iodine	ITO / bzn	+1.6 vs. Ag/Ag^+	44 (273K)
5.40	thiophene (0.2M)	Bu_4NClO_4 (0.02M)	ClO_4^-	Pt / nbz / 5°C / Ar	+2.02 (CV)	40 (film)
5.41	thiophene (0.4M)	$LiBF_4$ (0.5M)	BF_4^-	ITO / bzn / 30°C	+2.0	106
5.42	2,2'-bithiophene (0.01M)	$LiClO_4$ (0.1M)	ClO_4^-	Pt / acn(anhyd) / Ar	+0.7 vs. Ag/Ag^+	0.04
5.40	2,2'-bithiophene (0.2M)	Bu_4NPF_4 (0.5M)	PF_4^-	Pt / acn	+1.32 (CV)	0.6 (pellet)
5.34	2,2'-bithiophene	Et_4NBF_4 (0.5M)	BF_4^-	Pt / acn	+1.1 (CV)	10^{-4} (film)
5.35	2,3'-bithiophene	Et_4NBF_4 (0.5M)	---	Pt / acn	+1.1 (CV)	---
5.40	trithiophene (66mM)	Bu_4NClO_4 (0.02M)	ClO_4^-	Pt / nbz / 5°C / Ar	+1.05 (CV)	0.005 (pellet)
5.40	trithiophene (0.01M)	H_2SO_4 (0.1M)	SO_4^{2-}	ITO / acn	1mA cm^{-1}	0.02 (gel)
5.40	trithiophene (0.01M)	Bu_4HSO_4 (0.1M)	HSO_4^-	ITO / nmp	1mA cm^{-1}	10^{-8} (film)

Electrochemical synthesis of polythiophenes.

[a] Potentials measured vs. SCE, if current density only quoted in original ref. this is in place of potential.

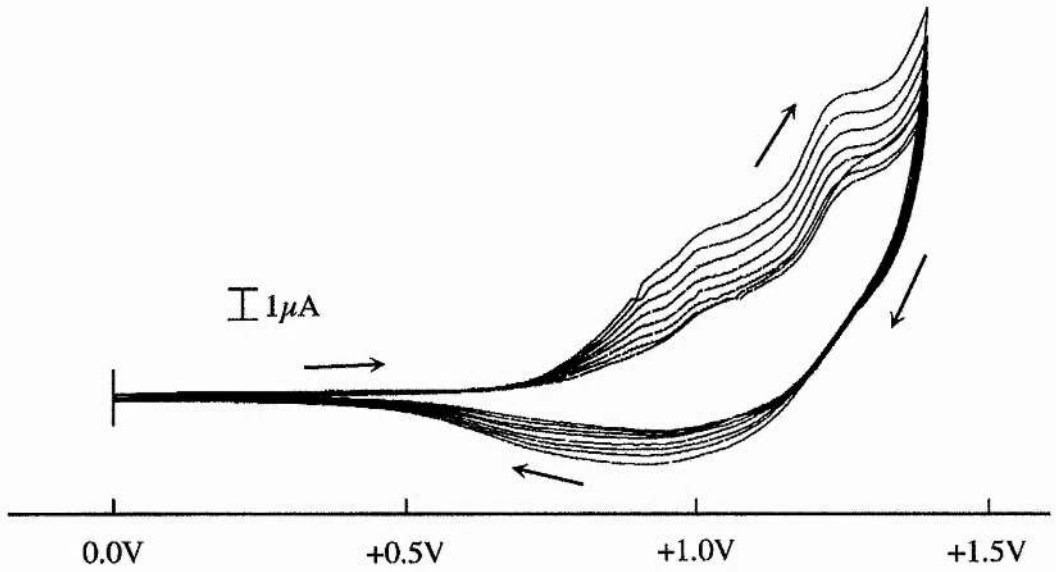
Table 5.2

Polythiophene can be both p- and n-doped, although the n-doped material has a lower maximum conductivity[5.51]. The cyclic voltammogram of polythiophene shows two sets of peaks with E^0 values at +1.1V and -1.4V (vs. Ag^+/Ag). These values are in agreement with the theoretical calculations of Bredas *et. al.*[5.52], and as expected for a surface-reacting species the peak anodic current increase linearly with sweep rate. Polythiophene and derivatives essentially behave similarly in both aqueous and organic solvents, with only a few noticeable differences. In organic solvents the polymers are only stable up to +0.8V vs. SCE, and the initial cycle does not appear to be completely reversible[5.53]. The peaks observed in the cyclic voltammogram are somewhat broader than would be expected for a simple Nernstian reaction[5.50] this is most likely to be due to the difference in solvent uptake.

5.5 Electrochemistry of Oligo- and Poly-thiophenes

As mentioned previously the electrochemistry of polythiophene has been extensively studied. In this section we confirm the similarities between the reported electrochemical data and the data obtained from our own studies. The electrochemical studies of these monomers and polymers is being fully investigated by other members of the group and will be reported elsewhere, thus only a brief summary of some of the important results will be discussed.

The two soluble α-sexithiophenes, prepared by the simple cupric chloride homocoupling of the lithiated derivatives of the terthiophenes[5.54], essentially showed similar electrochemistry. The electrochemical coupling of β',β''''-didecyl-2,2';5',2'';5'',2''';5''',2'''';5'''',2'''''-sexithiophene has been investigated by Garnier *et. al.*[5.55]. Our results confirm and agree with those reported. Figure 5.6 outlines the CV for the electrocoupling of a low concentration of the fully conjugated monomer, β',β''''-dihexyl-2,2';5',2'';5'',2''';5''',2'''';5'''',2'''''-sexithiophene,

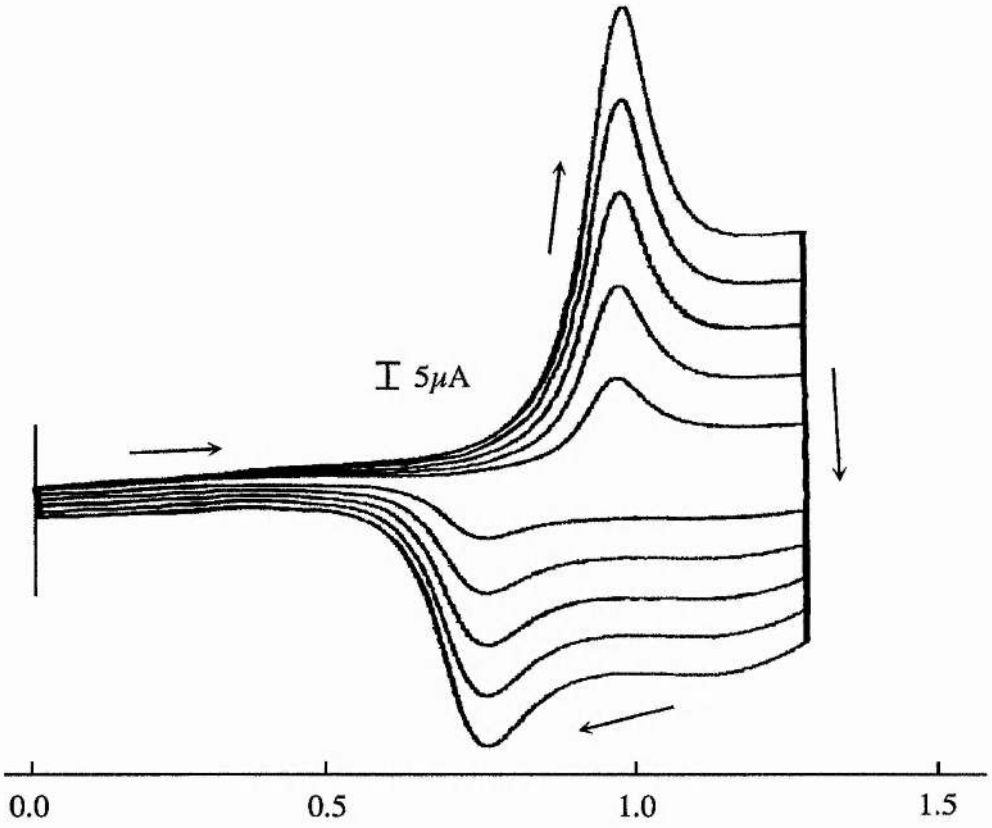


CV for 5mM β',β''''-dihexyl-2,2';5',2'';5'',2''';5''',2'''';5'''',2''''' -sexithiophene in MeCN / 0.1M TBAT. Electropolymerisation at 100mV/s.

Figure 5.6

in acetonitrile / 0.1M TBAT. Similar to Garnier *et. al.*[5.55], we see two major quasi-reversible systems which can be assigned to the successive formation of the oligomer radical cation and dication. After several cycles all the voltammetric signals start to increase steadily, including some new peaks, which only appeared after a few cycles.It can be assumed that these peaks are due to a new electroactive species being formed during the cyclisation process.

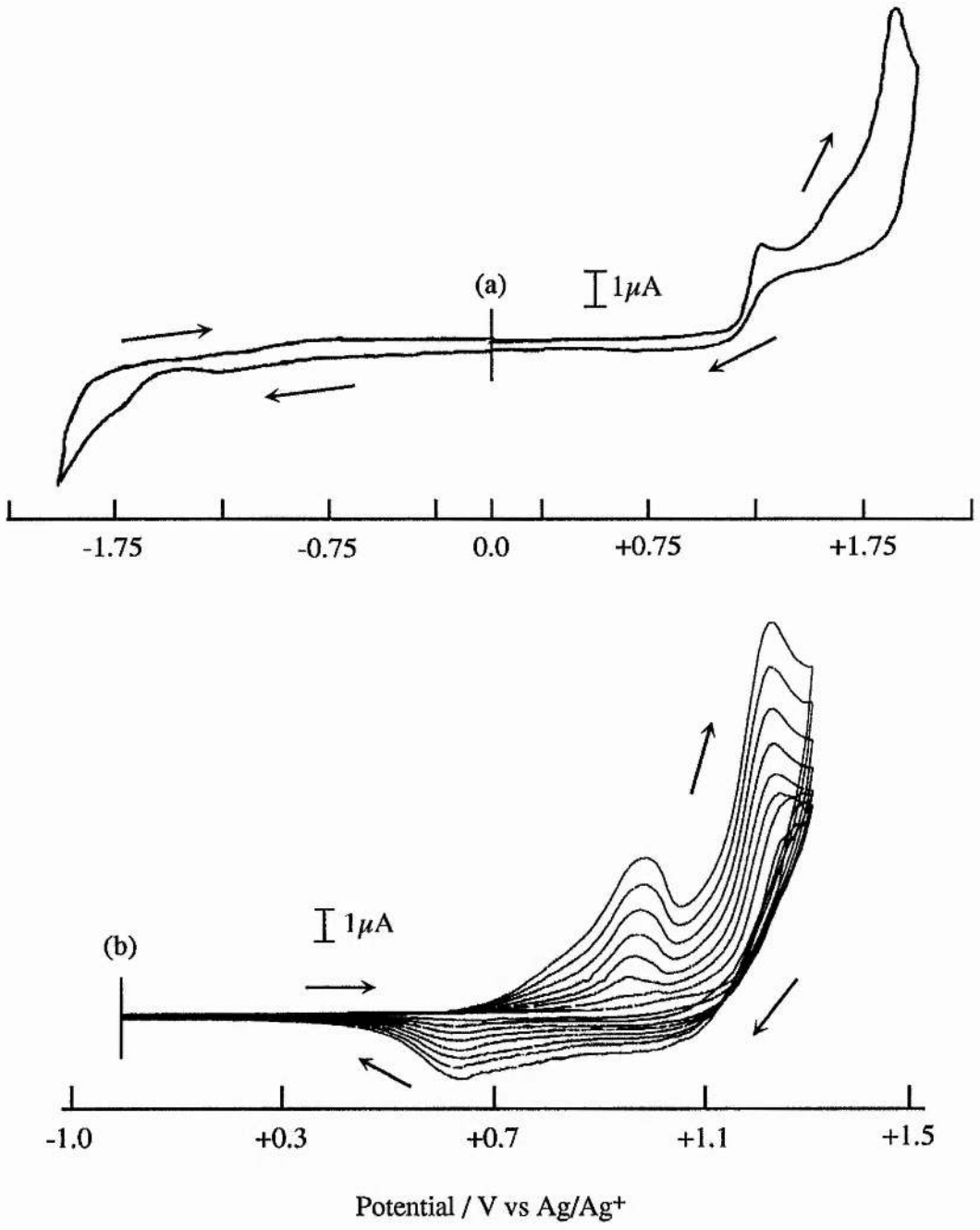
Upon removal of the working electrode from the electrochemical cell it was noticed that a black residue had precipitated on the surface. This black powder, most likely a cation salt of the oligomer, was removed by careful washing to afford the polymer coated electrode. The polymer appeared as a thin film with a deep red colour



CV for electrocoupled β',β''''-dihexyl-2,2';5',2'';5'',2''';5''',2'''';
5'''',2''''' -sexithiophene adsorbed onto platinum in fresh MeCN /
0.1M TBAT, for scan rates 20-100mV/s.

Figure 5.7

at 0.0V and a light blue film at +0.8V. The voltammogram, Figure 5.7, obtained by cycling the polymer in monomer free electrolyte is typical of conducting polymers. The peak potentials correspond with those reported for the best polythiophene films[5.56]. It is also noted that the peak width is narrow, suggesting complete homogeneous conjugation along the polymer chain. We also see the characteristic plateau[5.57] and a potential hysteresis (ΔE_p = 165mV). These two features are due to the large number of adjacent redox states in the long conjugated chains and the



CV for 10mM 3'-hexyl-2,2';5',2''-terthiophene in MeCN / 0.1M TBAT, scan rate 100mV/s: (a) First scan; and (b) Electropolymerisation, scans 2 to 8, with anodic limit +1.3V.

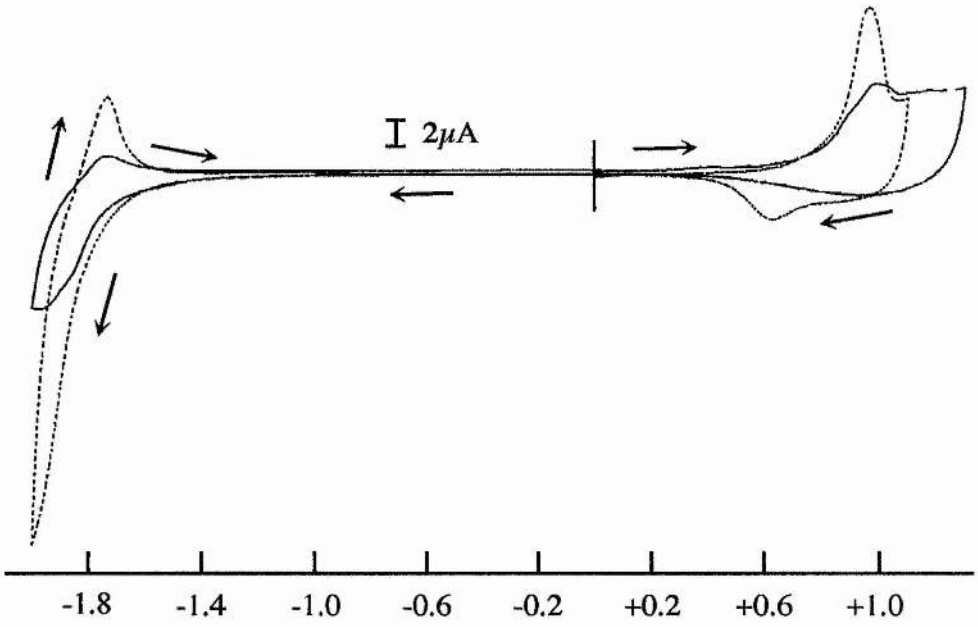
Figure 5.8

conformational relaxation of chains between the planar cationic state and the flexible neutral states respectively[5.58].

As a comparison we electropolymerised the trimer 3'-hexyl-2,2';5',2''-terthiophene using similar conditions as used above for the α-sexithiophene. Figure 5.8(a) details the first scan, in acetonitrile / 0.1M TBAT, with an anodic limit of +2.0V. We see two anodic peaks at +1.25V and +1.90V. Upon applying an anodic limit of +1.3V, we start to see a build up in current due to the electropolymerisation - Figure 5.8(b). Along with the increase of the anodic peak at +1.25V, we also start to see the emergence of another two peaks, E_p^a +0.97V and E_p^c +0.65V. The two CVs for the obtained polymers from the trimer and seximer, in monomer free solution are compared in Figure 5.9. It is noted that they have remarkably similar doping potentials, especially for n-doping. The CV for the trimer gives particularly sharp peaks. The reason for this is not known for certainty, but perhaps the trimer forms a more regular polymers.

The preliminary results for the two α-quinquethiophenes are essentially the same as those for the α-sexithiophenes. The initial results for the electropolymerisation of the two α-quinquethiophenes show similar peak potentials and similar cyclic voltammograms. We note only slight differences in the peak potentials (0.5%). This will be due to the twisting of the thiophene rings out of coplanarity, and hence altering the conductance of the chain. Thus one can assume that the addition of side alkyl chains only play a small part in the overall conductance of the polymer. The solubility of the monomer is more important as this enables the polymerisation to proceed more easily.

The electropolymerisation of the monomer 3-(3-phenylpropyl)thiophene in MeCN / 0.1M TBAT is detailed in Figure 5.10. The optical and magnetic properties the polymer prepared by chemical polymerisation of this monomer have been briefly

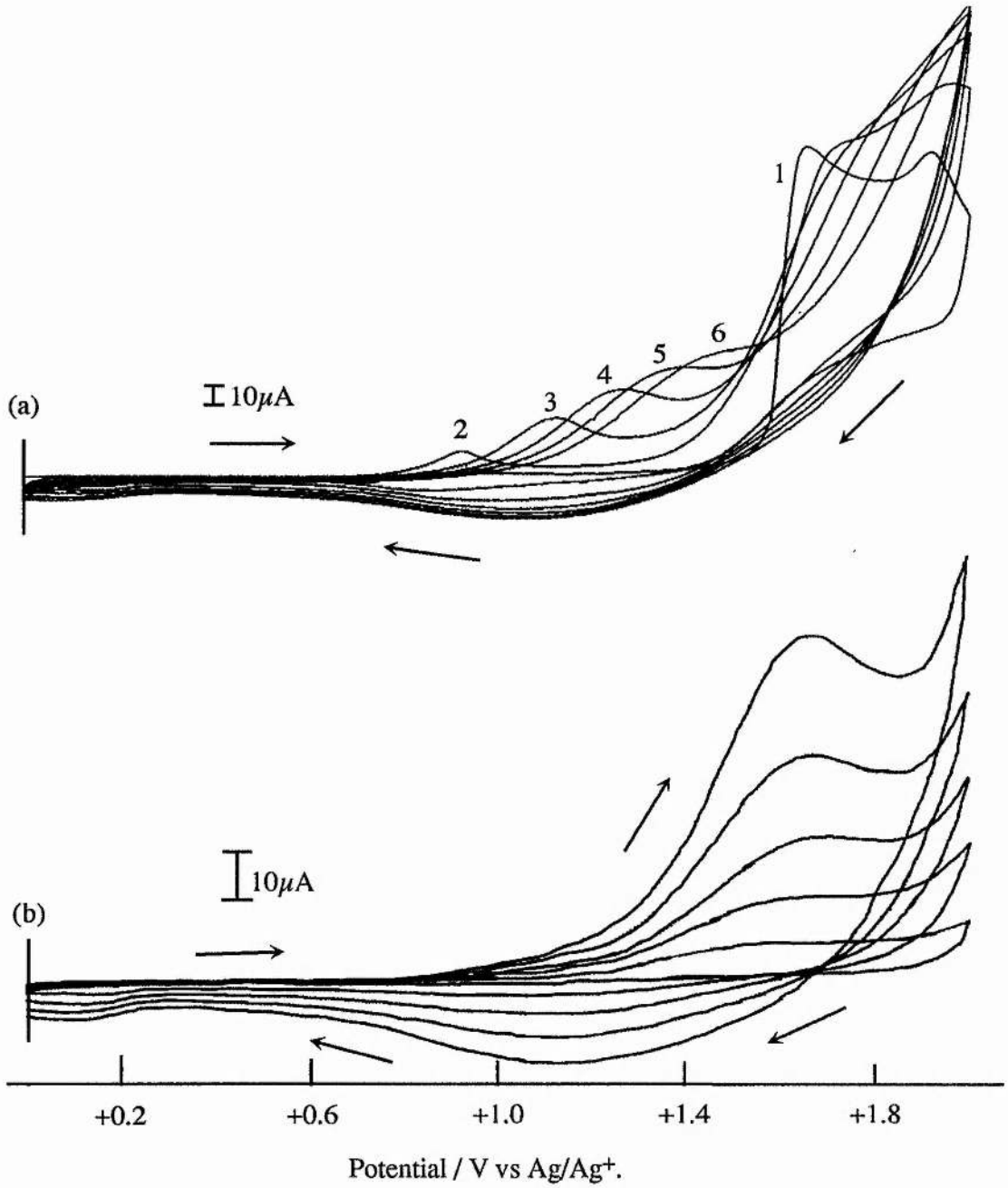


Comparison of the CV's for the two polymers from the trimer (- - -) and the seximer (——) in monomer free MeCN / 0.1M TBAT, scan rate 100mV/s.

Figure 5.9

studied by Onoda *et. al.*[5.59]. For the first time we report the electrochemical polymerisation of the monomer 3-(3-phenylpropyl)thiophene). Figure 5.10(a) details the first five scans, within the voltage range 0.0V to +2.0V. The first scan shows two anodic peaks at +1.6V and +1.95V. This is characteristic of the electropolymerisation of thiophene[5.60], and describes the first stage in the nucleation procedure.

Further scans numbered 2 to 6 are also shown in Figure 5.10(a). We start to see a steady build up of current, corresponding to the growth of the polymer. It is also noted that the film is more conductive at low coverages, as shown by the positive shift in the peak. This is well known for the electropolymerisation of substituted



CV for 10mM 3-(3-phenylpropyl)thiophene in MeCN / 0.1M TBAT: (a) Electropolymerisation, scans 1 to 6; and (b) Polymer in monomer free solution, scan rates 20-100mV/s.

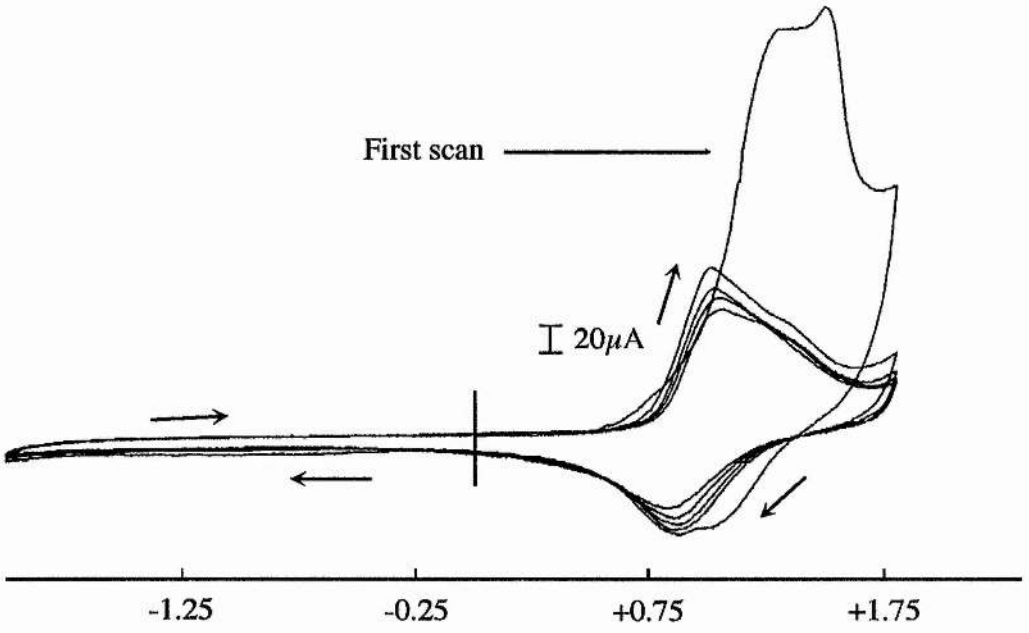
Figure 5.10

polythiophenes[5.61]. This positive shift stops after 15 scans at +1.55V. After this we see no further increase in the current. Visual examination of the electrode confirms the presence of a polymer as a black film. Figure 5.10(b), the polymer coated electrode in monomer free electrolyte, details both the anodic (+1.55V) and cathodic (+1.10V) peaks whose heights increase approximately linearly with increase in scan rates.

The results obtained for these oligothiophenes supports the nucleation mechanism for the formation of conducting polymer chains[5.62]. This assumption is based on the formation of the black precipitated residue of oligomers found on the electrode surface. Roncali *et. al.*[5.63] established that a high monomer concentration would induce the formation of a large number of oligomers near the film and that these species, when incorporated into the film would have negative effects on the quality of the polymer film. Taking this into account and from our own results, it seems reasonable to predict that dilution, of the monomer would favour the adsorption of longer oligomers onto the electrode surface and that the quality of the films should be better through nucleation and further precipitation of these longer oligomers.

The preliminary results for the electrochemistry for the three poly((3-alkyl)thiophenes) confirm that these polymers are comparable with those previously reported by M^{C}Cullough *et. al.*[5.64]. Figure 5.11 outlines the CV obtained for the structurally homogeneous poly((3-octyl)thiophene) in acetonitrile / 0.1M TBAT. A film of the red-brown polymer was deposited on the electrode by placing a 1μL drop of a weak dichloromethane solution of the polymer onto the tip of the carbon electrode. After evaporation of the solvent, a dull film could be seen on the electrode surface.

The first scan, which at first seems erratic, can easily be attributed to the solvation and introduction of the electrolyte into the polymer structure. The second and subsequent scans, show stabilisation of the polymer and two peaks at E_p^a +1.05V



CV for chemically prepared poly((3-octyl)thiophene) coated carbon electrode in MeCN / 0.1M TBAT. Scans 1 to 5 at 100mV/s.

Figure 5.11

and E_p^c +0.86V. These peaks are comparable with those reported by Zagórska and Krische[5.65]. The polymer in this case was prepared by the $FeCl_3$ method[5.66] and deposited on the electrode by spin coating. They report peak potentials of E_p^a +0.95V and E_p^c +0.70V. These peaks are at a slightly lower peak potential than recorded for our polymer and have a larger peak separation ΔE 250mV compared to ΔE 190mV for our well defined chemically prepared polymer. The lower potential could be attributed to the different solvent / electrolyte system. The difference in the peak separation is what we would expect. The head-to-tail arrangement in our polymer gives rise to a larger number of closely adjacent redox states and hence the conjugation along this well defined polymer is superior.

5.6 Summary and Conclusions

Polymers were once considered as solely insulating compounds. Since the unexpected discovery of the conducting properties of polyacetylene the study of the electronic properties of a wide range of polymers has now been studied. Of these various conducting polymers, polythiophene has been one of the most extensively studied. This Chapter details my investigations into the electrochemistry of polythiophene. Firstly, a brief summary of the principles of electrochemistry, particularly the usefulness of cyclic voltammetry is outlined. This is followed by a description of the experimental electrochemical cell, and a detailed literature review. Finally, the primary results from the electrochemical studies of some of the oligothiophenes and the polythiophene are discussed.

The electrochemistry of the oligothiophenes essentially show similar results. From the cyclic voltammograms we can confirm that the electropolymerisation proceeds via a nucleation mechanism. The formation of a black residue around the electrode helps to confirm this. We propose that this residue contains various cationic salts of the oligomers. We see two major quasi-reversible peaks that can be easily assigned to the formation of the cation and dication successively. It is also noted that the peak width, as shown in Figure 5.7, is narrow. This is due to the complete homogeneous conjugation along the polymer chain length. The peak widths and the peak potentials deviate only slightly depending on which oligothiophenes we are studying. These slight differences are due to the twisting of the thiophene rings out of coplanarity, upon substitution with various side chains.

The electrochemistry of the chemically prepared, well defined poly((3-alkyl)thiophenes) is also briefly investigated. By comparison to other methods of polymerisation we see that our polymer has similar peak potentials. The main difference is that our polymers give somewhat sharper peaks in the CV. This is

indicative of a more conjugated system, and helps to reinforce the NMR data, as discussed in Chapter 4, indicating that our polymers have a high yield of head-to-tail couplings.

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Appendix One

X-Ray Structure Report for 2,5-di-(2-thienyl) pyridine

Data Collection

A yellow needle crystal of $C_{13}H_9NS_2$ having approximate dimensions of 0.45 x 0.30 x 0.15 mm was mounted on a glass fiber. All measurements were made on Rigaku AFC7S diffractomter with graphite monochomated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range $23.61 < 2\vartheta < 27.37^o$ corresponded to a primitive monoclinic with dimensions:

$a = 5.999(1)$ Å

$b = 20.455(4)$ Å $\qquad B = 92.77(1)^o$

$c = 13.966(1)$ Å

$V = 1711.7(4)$ Å^3

For Z = 6 and F.W. = 243.34, the calculated density is 1.42 g/cm^3. The systematic absences of:

$h01: \; 1 \neq 2n$

$0k0: \; k \neq 2n$

uniquely determine the space group to be:

$P2_1/c$ (#14)

The data were collected at a temperature of 20 ± 1°C using the ω-2ϑ scan

technique to a maximum 2ϑ value of 50.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.28° with a take-off angle of 6.0°. Scans of $(1.73 + 0.35 \tan \vartheta)^\circ$ were made at a speed of 16.0° / min (in omega). The weak reflection ($I < 15.0\sigma(I)$) were rescaned (maximum of 4 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time was 2:1. The diameter of the incident beam collimator was 1.0mm and the crystal to detector distance was 235mm. The computer-controlled slits were set to 9.0mm (horizontal) and 13.0 mm (vertical).

Data Reduction

Of the 3424 reflections which were collected, 3112 were unique ($R_{int} = 0.044$). The intensities of three representative reflection were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ, for Mo-Kα radiation is 4.3 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement[3] was based on 1728 observed reflections ($I > 3.00\sigma(I)$) and 217 variable parameters and converged (largest parameter shift was 0.05 times its esd) with

unweighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.083$$

$$R\omega = \sqrt{(\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)} = 0.075$$

The standard deviation of an observation of unit weight[4] was 4.30. The weighting scheme was based on counting statistics. Plots of $\Sigma\omega(|F_o| - |F_c|)^2$ verses $|F_o|$, reflection order in data collection, sin ϑ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.57 and -0.55 $e^- {}^oÅ^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the value for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubble[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

Experimental Details - Crystal Data

Empirical Formula	$C_{13}H_9NS_2$
Formula Weight	243.34
Crystal Colour, Habit	yellow, needle
Crystal Dimensions	0.45 x 0.30 x 0.15 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Dimensions	25 (23.6 - 27.4°)
Omega Scan Peak Width	
at Half-Height	0.28°

Lattice Parameters	a = 5.999(1) Å
	b = 20.455(4) Å
	c = 13.966(1) Å
	β = 92.77(1) ^{o}
	V = 1711.7(4) Å^3
Space Group	$P2_1$ / c (#14)
Z value	6
D_{calc}	1.416 gcm^{-3}
F_{ooo}	756.00
μ(Mo-Kα)	4.34 cm^{-1}

Experimental Details - Intensity Measurements

Diffractomter	Rigaku AFC7S
Radiation	Mo-Kα (λ = 0.71069 Å)
	graphite monochromated
Attenuator	Zr foil (factors=1.00, 8.53, 8.53, 8.53)
Take-off Angle	6.0^{o}
Detector Aperture	9.0 mm horizontal
	13.0 mm vertical
Crystal to Detector Distance	235 mm
Temperature	20.0^{o}C
Scan Type	ω - 2ϑ
Scan Rate	16.0^{o}/ min (in ω) (up to 4 scans)
Scan Width	(1.73 + 0.35 tan ϑ)^{o}
$2\vartheta_{max}$	50.0^{o}
No. of Reflections Measured	Total:- 3424
	Unique:- 3112 (R_{int} = 0.044)

Corrections	Lorentz-polarization

Experimental Details - Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinements	Full-matrix least-squares
Function Minimised	$\sum\omega(\|F_o\| - \|F_c\|)^2$
Least Squares Weight	$[1] / [\sigma^2(F_o)] = [4F_o^2] / [\sigma^2(F_o^2)]$
p-factor	0.000
Anomalous Dispersion	All non-hydrogens
No. Observations ($I > 3.00\sigma(I)$)	1728
No. Variables	217
Reflection / Parameter Ratio	7.96
Residuals: R; Rw	0.083; 0.075
Goodness of Fit Indicator	4.30
Max Shift / Error in Final Cycle	0.05
Max peak in Final Diff. Map	0.57 e^- / Å^3
Min peak in Final Diff. Map	-0.55 e^- / Å^3

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(3) Least-Squares:-

Function minimised:- $\sum\omega(|F_o| - |F_c|)^2$

where $\omega = [1] / [\sigma^2(F_o)] = [4F_o^2] / [\sigma^2(F_o^2)]$

$$\sigma^2(F_o^2) = [s^2(C+R^2B)+(pF_o^2)^2] / [Lp^2]$$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

Lp = Lorentz-polarization factor

p = p-factor

(4) Standard deviation of an observation of unit weight:-

$$\sqrt{\Sigma\omega(|F_o| - |F_c|)^2/(N_o - N_v)}$$

where N_o = number of observations

N_v = number of variables

(5) D.T. Cromer & J.T. Waber, *International Tables for X-ray Crystallography*, Vol IV, The Kynoch Press, Birmingham, England, 1974, Table 2.2A.

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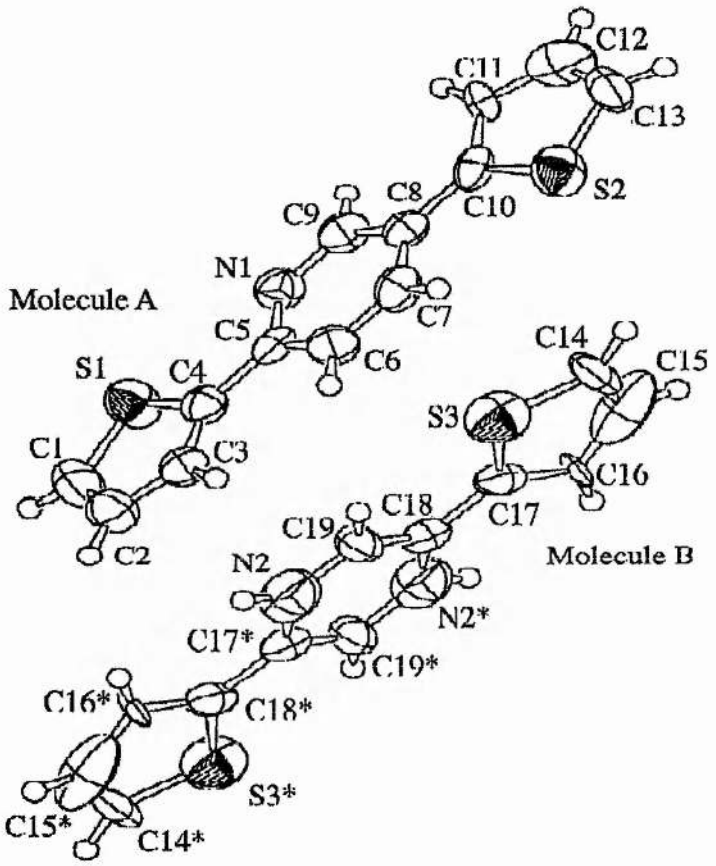
(8) D.C. Creagh & J.H. Hubbell, *International Tables for Crystallography*, Vol C. Eds.- A.J.C. Wilson, Kluwer Academic Publishers, Boston, 1992, Table 4.2.4.3, pages 200-206.

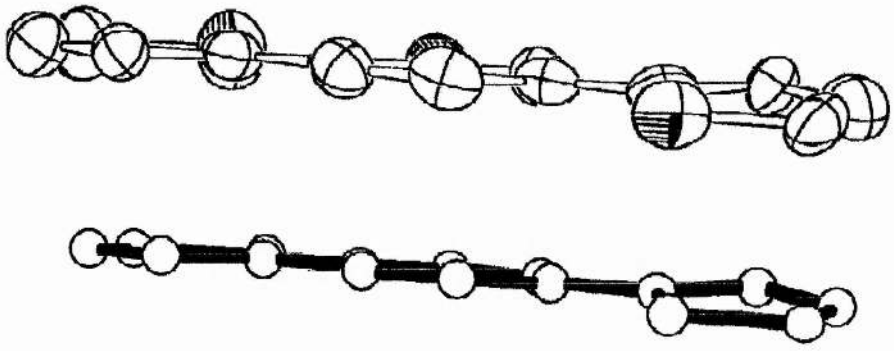
(9) teXsan:- Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992)

Reported by:- Dr. Philip Lightfoot.



The X-ray structure of the monomer 2,5-di-(2-thienyl) pyridine (3.17), showing the two possible isomers.

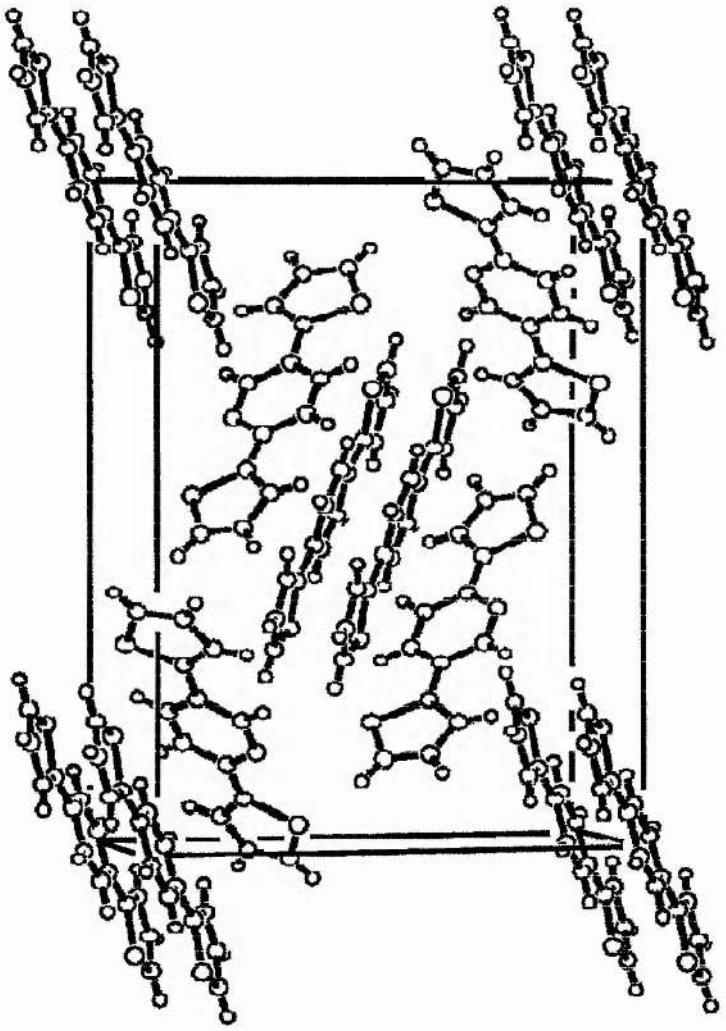
Figure 3.20



The X-ray structure of 2,5-di-(2-thienyl) pyridine (3.17).

Side on view showing the extent of the puckering.

Figure 3.21



The X-ray structure of the monomer 2,5-di-(2-thienyl) pyridine (3.17), showing stacking in the normal herringbone pattern.

Figure 3.22

atom	x	y	z	B_{eq}
S(1)	0.5078(4)	0.0308(1)	0.6454(2)	5.41(7)
S(2)	0.7674(4)	0.3126(1)	1.0310(2)	5.75(7)
S(3)	0.1145(5)	0.1784(2)	1.1053(2)	6.93(8)
N(1)	0.694(1)	0.1431(3)	0.7569(5)	4.2(3)
N(2)	- 0.203(1)	0.0102(5)	0.9588(6)	6.8(3)
C(1)	0.296(2)	- 0.0235(5)	0.6328(7)	5.6(3)
C(2)	0.141(1)	- 0.0139(5)	0.6975(7)	5.1(3)
C(3)	0.190(1)	0.0377(4)	0.7602(6)	3.8(2)
C(4)	0.388(1)	0.0678(4)	0.7407(5)	3.7(2)
C(5)	0.498(1)	0.1222(4)	0.7897(5)	3.4(2)
C(6)	0.411(1)	0.1526(4)	0.8679(6)	4.4(2)
C(7)	0.520(1)	0.2036(4)	0.9121(5)	4.3(2)
C(8)	0.723(1)	0.2255(4)	0.8802(5)	3.3(2)
C(9)	0.800(1)	0.1931(4)	0.8015(5)	3.9(2)
C(10)	0.851(1)	0.2792(4)	0.9247(5)	3.8(2)
C(11)	1.052(1)	0.3089(4)	0.8927(5)	2.9(2)
C(12)	1.121(1)	0.3550(5)	0.9620(8)	6.4(3)
C(13)	0.993(2)	0.3636(4)	1.0380(7)	5.3(3)
C(14)	0.345(2)	0.2059(5)	1.1703(6)	6.2(3)
C(15)	0.490(2)	0.1572(8)	1.1867(8)	8.9(4)
C(16)	0.438(1)	0.0964(4)	1.1553(5)	2.5(2)
C(17)	0.230(1)	0.1024(4)	1.1041(5)	4.0(2)

Atomic coordinates and B_{iso}/B_{eq}.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.1

atom	x	y	z	B_{eq}
C(18)	0.107(1)	0.0517(4)	1.0505(6)	3.7(2)
C(19)	- 0.096(1)	0.0597(4)	1.0079(6)	4.1(2)
H(1)	0.2881	- 0.0570	0.5856	6.7208
H(2)	0.0103	- 0.0399	0.7003	6.0710
H(3)	0.0972	0.0507	0.8102	4.5778
H(4)	0.2733	0.1378	0.8910	5.2357
H(5)	0.4571	0.2244	0.9653	5.1523
H(6)	0.9368	0.2073	0.7773	4.7122
H(7)	1.1240	0.2990	0.8354	3.5308
H(8)	1.2541	0.3796	0.9557	7.6379
H(9)	1.0238	0.3938	1.0885	6.3298
H(10)	0.3666	0.2497	1.1915	7.4160
H(11)	0.6291	0.1654	1.2204	10.6129
H(12)	0.5237	0.0578	1.1655	2.9875
H(13)	- 0.1670	0.1010	1.0118	4.8410
H(14)	- 0.3464	0.0175	0.9286	8.1228

$$B_{eq} = (8/3)\pi^2 [U_{11} (aa^*)^2 + U_{22} (bb^*)^2 + U_{33} (cc^*)^2 + 2U_{12} aa^*bb^* \cos\gamma + 2U_{13} aa^*cc^* \cos\beta + 2U_{23} bb^*cc^* \cos\alpha]$$

Atomic coordinates and B_{iso}/B_{eq}.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.1 (cont)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.069(2)	0.071(2)	0.066(2)	- 0.006(1)	0.015(1)	- 0.017(1)
S(2)	0.086(2)	0.068(2)	0.064(2)	0.009(2)	0.003(1)	- 0.012(1)
S(3)	0.101(2)	0.076(2)	0.087(2)	0.012(2)	0.015(2)	0.002(2)
N(1)	0.058(5)	0.053(5)	0.049(4)	- 0.001(4)	0.012(4)	0.000(4)
N(2)	0.076(6)	0.104(8)	0.077(6)	- 0.003(6)	0.005(5)	0.019(6)
C(1)	0.077(7)	0.063(7)	0.072(7)	- 0.006(6)	- 0.007(6)	- 0.016(6)
C(2)	0.054(6)	0.066(7)	0.072(7)	- 0.012(5)	- 0.008(5)	0.007(6)
C(3)	0.049(5)	0.044(5)	0.052(5)	0.007(4)	0.002(4)	0.006(4)
C(4)	0.055(5)	0.040(5)	0.045(5)	0.007(4)	0.002(4)	0.004(4)
C(5)	0.055(5)	0.042(5)	0.031(4)	0.011(4)	0.006(4)	0.011(4)
C(6)	0.050(5)	0.062(6)	0.055(6)	- 0.007(5)	0.012(4)	0.003(5)
C(7)	0.062(6)	0.065(6)	0.038(5)	0.006(5)	0.014(4)	- 0.003(5)
C(8)	0.045(5)	0.037(5)	0.042(5)	0.010(4)	0.004(4)	0.007(4)
C(9)	0.047(5)	0.056(6)	0.048(5)	0.003(4)	0.017(4)	0.006(5)
C(10)	0.058(5)	0.050(6)	0.034(4)	0.020(5)	- 0.005(4)	0.002(4)
C(11)	0.036(4)	0.039(5)	0.037(4)	0.002(4)	- 0.004(3)	- 0.015(4)
C(12)	0.046(6)	0.092(9)	0.104(8)	0.003(6)	0.011(6)	0.025(7)
C(13)	0.071(6)	0.051(6)	0.075(7)	- 0.001(5)	- 0.032(5)	- 0.009(5)
C(14)	0.105(8)	0.086(8)	0.047(6)	- 0.069(7)	0.027(6)	- 0.031(6)
C(15)	0.043(6)	0.22(2)	0.077(8)	0.036(9)	0.004(6)	0.06(1)
C(16)	0.025(4)	0.022(4)	0.045(5)	- 0.002(3)	- 0.020(3)	- 0.012(4)
C(17)	0.075(6)	0.034(5)	0.044(5)	- 0.006(5)	0.024(4)	0.001(4)

Anisotropic displacement parameters.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.2

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(18)	0.057(6)	0.037(5)	0.046(5)	0.006(4)	0.012(4)	0.011(4)
C(19)	0.054(6)	0.040(5)	0.059(6)	- 0.003(5)	- 0.006(5)	- 0.003(5)

The general temperature factor expression:-

$$\exp [-2\pi^2 (a^{*2} U_{11} h^2 + b^{*2} U_{22} k^2 + c^{*2} U_{33} l^2 + 2a^*b^* U_{12} hk + 2a^*c^* U_{13} hl + 2b^*c^* U_{23} kl)]$$

Anisotropic displacement parameters.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.2 (cont)

atom	atom	distance	atom	atom	distance
S(1)	C(1)	1.689(9)	C(5)	C(6)	1.38(1)
S(1)	C(4)	1.717(8)	C(6)	C(7)	1.37(1)
S(2)	C(10)	1.731(8)	C(7)	C(8)	1.39(1)
S(2)	C(13)	1.706(9)	C(8)	C(9)	1.38(1)
S(3)	C(14)	1.713(9)	C(8)	C(10)	1.46(1)
S(3)	C(17)	1.702(8)	C(10)	C(11)	1.44(1)
N(1)	C(5)	1.350(9)	C(11)	C(12)	1.40(1)
N(1)	C(9)	1.342(1)	C(12)	C(13)	1.35(1)
N(2)	C(18)	1.40(1)	C(14)	C(15)	1.34(1)
N(2)	C(19)	1.37(1)	C(15)	C(16)	1.35(2)
C(1)	C(2)	1.34(1)	C(16)	C(17)	1.41(1)
C(2)	C(3)	1.39(1)	C(17)	C(18)	1.46(1)
C(3)	C(4)	1.38(1)	C(18)	C(19)	1.33(1)
C(4)	C(5)	1.45(1)			

Intramolecular distances(angstroms) involving the nonhydrogen atoms.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.3

atom	atom	distance	atom	atom	distance
N(2)	H(14)	0.951	C(11)	H(7)	0.950
C(1)	H(1)	0.951	C(12)	H(8)	0.950
C(2)	H(2)	0.950	C(13)	H(9)	0.950
C(3)	H(3)	0.950	C(14)	H(10)	0.950
C(6)	H(4)	0.950	C(15)	H(11)	0.951
C(7)	H(5)	0.950	C(16)	H(12)	0.950
C(9)	H(6)	0.950	C(19)	H(13)	0.951

Intramolecular distances(angstroms) involving the hydrogen atoms.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.4

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	S(1)	C(4)	91.7(4)	C(9)	C(8)	C(10)	120.6(7)
C(10)	S(2)	C(13)	91.6(4)	N(1)	C(9)	C(8)	124.6(7)
C(14)	S(3)	C(17)	89.3(5)	S(2)	C(10)	C(8)	119.4(6)
C(5)	N(1)	C(9)	118.9(7)	S(2)	C(10)	C(11)	112.5(6)
C(18)	N(2)	C(19)	121.9(8)	C(8)	C(10)	C(11)	128.0(7)
S(1)	C(1)	C(2)	112.1(7)	C(10)	C(11)	C(12)	107.1(7)
C(1)	C(2)	C(3)	113.7(8)	C(11)	C(12)	C(13)	117.9(9)
C(2)	C(3)	C(4)	111.7(7)	S(2)	C(13)	C(12)	110.8(7)
S(1)	C(4)	C(3)	110.7(6)	S(3)	C(14)	C(15)	110.4(9)
S(1)	C(4)	C(5)	120.5(6)	C(14)	C(15)	C(16)	119.4(1)
C(3)	C(4)	C(5)	128.8(7)	C(15)	C(16)	C(17)	105.7(7)
N(1)	C(5)	C(4)	117.8(7)	S(3)	C(17)	C(16)	115.0(6)
N(1)	C(5)	C(6)	119.7(8)	S(3)	C(17)	C(18)	117.2(7)
C(4)	C(5)	C(6)	122.5(7)	C(16)	C(17)	C(18)	127.8(7)
N(2)	C(18)	C(17)	119.2(8)	C(5)	C(6)	C(7)	120.6(8)
C(6)	C(7)	C(8)	120.7(7)	N(2)	C(18)	C(19)	116.1(8)
C(7)	C(8)	C(9)	115.5(7)	C(17)	C(18)	C(19)	124.7(8)
C(7)	C(8)	C(10)	123.8(7)	N(2)	C(19)	C(18)	122.0(8)

Intramolecular bond angles(°) involving the nonhydrogen atoms.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.5

atom	atom	atom	angle	atom	atom	atom	angle
C(18)	N(2)	H(14)	118.09	C(10)	C(11)	H(7)	126.44
C(19)	N(2)	H(14)	120.01	C(12)	C(11)	H(7)	126.45
S(1)	C(1)	H(1)	123.94	C(11)	C(12)	H(8)	121.05
C(2)	C(1)	H(1)	123.92	C(13)	C(12)	H(8)	121.05
C(1)	C(2)	H(2)	123.16	S(2)	C(13)	H(9)	124.56
C(3)	C(2)	H(2)	123.11	C(12)	C(13)	H(9)	124.60
C(2)	C(3)	H(3)	124.15	S(3)	C(14)	H(10)	124.69
C(4)	C(3)	H(3)	124.17	C(15)	C(14)	H(10)	124.88
C(5)	C(6)	H(4)	119.67	C(14)	C(15)	H(11)	120.09
C(7)	C(6)	H(4)	119.70	C(16)	C(15)	H(11)	120.47
C(6)	C(7)	H(5)	119.65	C(15)	C(16)	H(12)	127.11
C(8)	C(7)	H(5)	119.67	C(17)	C(16)	H(12)	127.17
N(1)	C(9)	H(6)	117.70	N(2)	C(19)	H(13)	119.02
C(8)	C(9)	H(6)	117.67	C(18)	C(19)	H(13)	118.98

Intramolecular bond angles(°) involving the hydrogen atoms.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.6

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
S(1)	C(1)	C(2)	C(3)	0(1)	S(1)	C(4)	C(3)	C(2)	0.0(9)
S(1)	C(4)	C(5)	N(1)	1.0(10)	S(1)	C(4)	C(5)	C(6)	-178.7(6)
S(2)	C(10)	C(8)	C(7)	7(1)	S(2)	C(10)	C(8)	C(9)	-172.8(6)
S(2)	C(10)	C(11)	C(12)	2.2(8)	S(2)	C(13)	C(12)	C(11)	0(1)
S(3)	C(14)	C(15)	C(16)	-2(1)	S(3)	C(17)	C(16)	C(15)	-3.6(10)
S(3)	C(17)	C(18)	N(2)	175.0(6)	S(3)	C(17)	C(18)	C(19)	-4(1)
N(1)	C(5)	C(4)	C(3)	180.0(6)	N(1)	C(5)	C(6)	C(7)	0(1)
N(1)	C(9)	C(8)	C(7)	0(1)	N(1)	C(9)	C(8)	C(10)	179.4(7)
N(2)	C(18)	C(17)	C(16)	4(1)	N(2)	C(19)	C(18)	C(17)	-179.9(8)
C(1)	S(1)	C(4)	C(3)	-0.2(7)	C(1)	S(1)	C(4)	C(5)	178.9(7)
C(1)	C(2)	C(3)	C(4)	0(1)	C(2)	C(1)	S(1)	C(4)	0.3(8)
C(2)	C(3)	C(4)	C(5)	-179.0(8)	C(3)	C(4)	C(5)	C(6)	0(1)
C(4)	C(5)	N(1)	C(9)	-179.6(7)	C(4)	C(5)	C(6)	C(7)	179.8(7)
C(5)	N(1)	C(9)	C(8)	0(1)	C(5)	C(6)	C(7)	C(8)	0(1)
C(6)	C(5)	N(1)	C(9)	0(1)	C(6)	C(7)	C(8)	C(9)	1(1)
C(6)	C(7)	C(8)	C(10)	-179.2(7)	C(7)	C(8)	C(10)	C(11)	-174.4(8)
C(8)	C(10)	S(2)	C(13)	176.6(6)	C(8)	C(10)	C(11)	C(12)	-175.9(8)
C(9)	C(8)	C(10)	C(11)	5(1)	C(10)	S(2)	C(13)	C(12)	0.6(8)
C(10)	C(11)	C(12)	C(13)	-1(1)	C(11)	C(10)	S(2)	C(13)	-1.6(6)
C(14)	S(3)	C(17)	C(16)	2.3(6)	C(14)	S(3)	C(17)	C(18)	-177.2(6)
C(14)	C(15)	C(16)	C(17)	3(1)	C(15)	C(14)	S(3)	C(17)	-0.2(8)
C(15)	C(16)	C(17)	C(18)	175.8(8)	C(16)	C(17)	C(18)	C(19)	176.2(8)

Torsion angles(°).

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.7

atom	atom	atom	atom	angle
C(17)	C(18)	N(2)	C(19)	179.9(7)

Torsion angles(°).

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.7 (cont)

atom	atom	distance	ADC	atom	atom	distance	ADC
S(1)	H(12)	3.216	65703	C(2)	H(9)	2.957	45404
S(1)	H(9)	3.349	45404	C(2)	H(11)	3.558	65703
S(1)	H(2)	3.398	65501	C(3)	H(12)	2.771	65703
S(1)	H(8)	3.507	45404	C(3)	H(9)	2.910	45404
S(1)	H(1)	3.546	65603	C(3)	H(14)	3.580	65501
S(1)	H(9)	3.582	55404	C(4)	H(12)	2.919	65703
S(2)	H(1)	3.135	65602	C(4)	H(9)	3.077	45404
S(2)	H(8)	3.486	45501	C(4)	H(14)	3.174	65501
S(2)	H(6)	3.563	4	C(5)	H(14)	3.007	65501
S(3)	H(5)	3.054	1	C(5)	H(10)	3.044	55404
S(3)	H(7)	3.244	45504	C(6)	H(10)	3.173	55404
S(3)	H(4)	3.291	1	C(6)	H(14)	3.217	65501
S(3)	H(11)	3.403	45501	C(6)	H(6)	3.256	45501
S(3)	H(6)	3.552	45504	C(6)	H(13)	3.328	65501
N(1)	H(10)	3.055	55404	C(6)	H(7)	3.473	45501
N(1)	H(3)	3.131	65501	C(7)	H(13)	3.099	65501
N(1)	H(9)	3.234	55404	C(7)	H(7)	3.219	45501
N(1)	H(14)	3.530	65501	C(7)	H(10)	3.314	55404
N(2)	H(3)	2.932	1	C(8)	H(11)	3.188	55404
N(2)	H(14)	3.242	45703	C(8)	H(13)	3.189	65501
N(2)	H(3)	3.488	55703	C(8)	H(10)	3.352	55404

Intermolecular distances(angstroms) involving the non-bonded contacts.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.8

atom	atom	distance	ADC	atom	atom	distance	ADC
N(2)	H(12)	3.525	45501	C(9)	H(10)	3.177	55404
C(1)	H(12)	3.050	65703	C(9)	H(4)	3.252	65501
C(1)	H(9)	3.161	45404	C(9)	H(11)	3.255	55404
C(1)	H(11)	3.569	65703	C(9)	H(3)	3.416	65501
C(2)	H(12)	2.853	65703	C(9)	H(13)	3.486	65501
C(10)	H(11)	3.292	55404	C(19)	H(12)	3.248	45501
C(10)	H(1)	3.455	65602	C(19)	H(3)	3.399	55703
C(11)	H(5)	3.112	65501	H(1)	H(8)	3.116	74602
C(11)	H(2)	3.368	65602	H(1)	H(9)	3.161	64602
C(11)	H(1)	3.442	65602	H(1)	H(11)	3.518	65703
C(11)	H(11)	3.451	55404	H(1)	H(8)	3.523	64602
C(12)	H(1)	3.091	65602	H(2)	H(8)	3.104	64602
C(12)	H(2)	3.194	65602	H(2)	H(12)	3.310	65703
C(12)	H(5)	3.346	65501	H(2)	H(9)	3.375	45404
C(13)	H(1)	2.860	65602	H(2)	H(7)	3.423	64602
C(14)	H(7)	2.717	45504	H(2)	H(11)	3.501	65703
C(14)	H(5)	2.996	1	H(3)	H(12)	3.183	65703
C(14)	H(6)	3.426	45504	H(3)	H(14)	3.271	1
C(15)	H(7)	3.223	45504	H(3)	H(9)	3.307	45404
C(15)	H(5)	3.382	1	H(3)	H(6)	3.371	45501
C(15)	H(13)	3.463	65501	H(3)	H(13)	3.454	1
C(16)	H(13)	3.177	65501	H(4)	H(6)	2.883	45501

Intermolecular distances(angstroms) involving the non-bonded contacts.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.8 (cont)

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
C(17)	H(4)	3.086	1	H(4)	H(13)	3.289	1
C(17)	H(2)	3.400	55703	H(4)	H(14)	3.379	65501
C(17)	H(5)	3.478	1	H(4)	H(7)	3.494	45501
C(18)	H(4)	3.047	1	H(5)	H(7)	3.044	45501
C(18)	H(3)	3.145	55703	H(5)	H(10)	3.273	1
C(18)	H(3)	3.354	1	H(5)	H(8)	3.401	45501
C(18)	H(2)	3.591	55703	H(5)	H(13)	3.425	65501
C(19)	H(3)	3.050	1	H(6)	H(10)	3.025	65404
C(19)	H(4)	3.235	1	H(6)	H(11)	3.267	55404
H(6)	H(9)	3.411	55404	H(7)	H(10)	2.726	65404
H(7)	H(11)	3.385	55404	H(7)	H(11)	3.572	65404
H(11)	H(13)	3.473	65501	H(12)	H(13)	3.036	65501
H(12)	H(14)	3.532	65501	H(14)	H(14)	2.871	45703
S(2)	N(1)	3.333(7)	4	C(2)	C(16)	3.60(1)	65703
S(2)	S(3)	3.570(4)	65501	C(7)	C(11)	3.54(1)	45501
S(3)	C(10)	3.567(8)	45501				

Intermolecular distances(angstroms) involving the non-bonded contacts.

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3.8 (cont)

(*) The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one digit numbers and one two digit number: TA(1st digit) + TB(2nd digit) + TC(3rd digit) + SN(4th and 5th digit). TA, TB, & TC are the crystal lattice translation digits along cell edges a, b, and c. A translation digit of 5 indicates the origin unit cell. If TA=4, this indicates a

translation of one unit cell length along the a axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus (+/-)4 lattice translations from the origin (TA=5,TB=5,TC=5) can be represented.

The SN or symmetry operator number refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of the symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell (TA=5,TB=5,TC=5) and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always ADC=55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of that atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (i.e. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1)	+X,	+Y,	+Z	(2)	-X,	1/2+Y,	1/2-Z
(3)	-X,	-Y,	-Z	(4)	+X,	1/2-Y,	1/2+Z